ABSTRACT

Title of Thesis: PERFORMANCE AND ENVIRONMENTAL ACCOUNTING OF AIR BIOFILTRATION FOR CARBON MONOXIDE REMOVAL

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The ability of air biofilters to remove carbon monoxide (CO), a priority pollutant that harms human and environmental health was investigated. Environmental accounting of biofilters was performed using emergy analysis to compare resource requirements of biofilters to catalytic converters. Cylindrical PVC biofilters were filled with pebbles or compost, inoculated with soil slurries and loaded with either bottled CO or engine exhaust CO. In batch experiments, compost and pebble biofilters exhibited exponential decrease in CO over time with compost removing 90% of 1000 ppm-bottled CO and pebble biofilters removing 80% CO in 24 hours. In continuous flow experiments, compost biofilter exposed to 1000 ppm-CO generated from a gasoline engine was able to reduce CO levels (45%) at efficiency commensurate to a bottled CO source. In the range of 500-1000 ppm-CO, biofilters used less total environmental and energy resources to remove CO (12E9 solar emjoules) than conventional catalytic converters (40E9 solar emjoules).

PERFORMANCE AND ENVIRONMENTAL ACCOUNTING OF AIR BIOFILTRATION FOR CARBON MONOXIDE REMOVAL

By

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Chapter 1: Introduction

1.1 Problem Statement

Carbon monoxide (CO) is a colorless, odorless, poisonous and tasteless gas that affects human health and the environment. CO is a byproduct of incomplete burning of any Carbon-based compound (OSHA, 2002). CO is easily absorbed into the bloodstream, where it combines with hemoglobin and forms Carboxyhemoglobin (COHb) (Raub et al, 1999). The presence of this compound in the blood reduces the oxygen carrying capacity to the body's organs and tissues (USEPA, 1995a). At low concentrations, CO can cause fatigue in healthy people and chest pain in people with heart disease (USEPA, 1995b). At higher contamination levels (COHb > 10%), it results in neurological symptoms like impaired vision and coordination, headaches, dizziness, confusion and nausea. (Raub et al, 2000). With extreme exposure, coma, convulsions and cardiopulmonary arrest may occur. CO exposure causes flu-like symptoms that clear up after leaving the contaminated area. (USEPA, 1995c). CO indoors contributes to bad indoor air quality, and is one of the causes of the "Sick Building Syndrome", where the occupants of a certain affected building repeatedly describe a complex range of vague and often subjective health complaints (Jones, 1999).

CO released to the atmosphere readily combines with and removes the OH^- radical present in the atmosphere through $OH^- + CO \rightarrow H^+ + CO_2$. The reaction with OH^- is a large sink for CO as it removes more than 80% of CO. The OH^- radical is

referred to as the "tropospheric vacuum cleaner" (Graedel, 1978) as it acts as a sink for hundreds of gases and reduces pollutant buildup (Thompson, 1992). Thus OH^- is the main oxidant in the atmosphere and its distribution determines the chemical sink of many trace constituents, including several greenhouse gases such as methane and ozone. (Moxley and Cape, 1996; Granier et al, 2000;). Thus CO released to the atmosphere, indirectly increases levels of O_3 and other volatile organic compounds by removing OH^- radical, which is the main atmospheric sink of the OH^- radical (Seiler, 1978; Zimmerman et al, 1978; Moxley and Smith, 1998; Granier et al, 2000). Hence CO, though radiatively unimportant, becomes a critical component in atmospheric chemistry because of the large effect it has on the hydroxyl radical (Conny, 1998). An increased tropospheric CO contributes to ground level Ozone levels (Watson et al, 1990). For each CO molecule reacting with OH^-, one molecule of O_3 could be formed (Logan et al, 1981). The indirect greenhouse warming effect due to increased CO levels is equivalent to the direct effects of increasing nitrous oxide (Daniel and Solomon, 1998). Thus CO, owing to its reactivity with OH^- is a critical component of atmospheric chemical systems and directly and indirectly affects numerous trace gases (Guthrie, 1989, Logan et al, 1981). Therefore CO levels play a key role in atmospheric chemistry and climate.

CO global emissions amount to about 2500 Tg $year^{-1}$ (Logan et al, 1981). CO presence in the outdoor environment is mainly due to incomplete and inefficient combustion of fossil fuels in automobiles and largely untreated industrial emissions (800-2000 Tg year-1). CO is produced by photochemical oxidation of methane (400-1000 Tg year-1) and Non-Methane Hydrocarbons (NMHC) (300-1200 Tg year-1).

Emissions from vegetation (50-130 Tg year-1) and photodecomposition of organic matter in surface waters (such as oceans, rivers, and lakes) and soil surface (20-80 Tg year-1) also contribute to global CO levels (Conrad, 1988, Logan et al, 1981). The main industrial producers of CO are ferrous and non ferrous metal processing industries, petroleum refineries and chemical industries.

CO is also a significant cause of indoor air pollution as well. Bad indoor air quality can lead to the "Sick Building Syndrome", where in the occupants experience discomforts like headache, dizziness, lethargy, which disappear on leaving the building. CO indoors can be attributed to gas cooking ranges, gas space heaters, Kerosene space heaters, environmental tobacco smoke, fireplaces and woodstoves. Operating vehicles in an attached, enclosed garage could also produce dangerous levels of CO indoors.

1.2 Current Methods for Controlling CO emissions

CO from automobile emissions is one major source of CO pollution. Therefore, the automotive catalytic converter is one of the most important means of controlling CO. The catalytic converter uses rare metals as catalysts to reduce nitric oxide (NO) to nitrogen gas and oxidize CO + hydrocarbons to CO_2 & water (Keith et al. 1969). This technique requires rare metals such as platinum, palladium or rhodium obtained from large-scale mining that consumes energy, degrades ecosystems and causes other indirect environmental impacts. Though efficiency of catalytic converters has been proved, it may not be sustainable and may cause other major environmental concerns. The average life of a catalytic converter is about 80000 miles, much less than the

expected life of a vehicle so older vehicles contribute to a higher proportion of atmospheric CO. Catalytic converters for automotive traction raise some concern for human health and the environment, due to the release of Pd, Pt and Rh (Platinum-Group Metals, PGMs). In fact, the thermal and mechanical conditions under which such devices work (including abrasion effects and hot-temperature chemical reactions with oil fumes) can cause significant release of the PGMs to the environment and eventually affect human health (Caroli et al, 2001).

1.3 Treatment of CO using Biofilters

Biological treatment methods use microbial metabolic activities to convert pollutants into harmless byproducts, like water, carbon dioxide and biomass. Microbial populations interact with a number of species symbiotically and bring about reduction in contaminant levels. Essentially the pollutants are broken down and used by microbes for metabolism. Therefore, bio-treatment seems to be a viable treatment process for biodegradable compounds with simple bond structures that are easily broken by microbes. With a favorable environment for microbial interactions, biological treatment processes can be a cost-effective and efficient method to degrade pollutants.

Microbial treatments have been used to treat solid waste since early twentieth century, but have been used to treat waste gases only since the fifties. The earliest biological treatments were soil beds that treated sewer gases (Carlson and Leiser, 1966) and the process was called biofiltration. Since then a variety of different media like wood chips, compost, activated carbon have been used to improve biofiltration

efficiency, clogging and head loss. Thus biofiltration uses active microbial communities immobilized on a wet and nutritious porous medium to degrade a variety of pollutants in a gaseous stream. Air biofilters work by creating a nutritional environment amenable to microbial transformations of waste elements and compounds.

Soil bed reactors and microbial air reactors have been demonstrated effective at reducing many organic and inorganic compounds in laboratory and commercial applications. Biofilters have been shown to remove contaminants like Diethyl ether (Yang et al, 2002), BTEX (Martinez and Tamara, 2002) and hydrogen sulfide (Jones et al, 2002). Soil bed reactors were found capable of removing odors of waste treatment plants (Carlson and Leiser, 1966). Smith et al (1973) demonstrated absorption capacities of sulfur dioxide, hydrogen sulfide, methyl mercapatan, and small amounts of ethylene, acetylene and carbon monoxide.

Though biofiltration for air quality management has been under investigation for several decades (DeVinney 1999), it has been only commercialized to a significant level in the last decade (Boswell et al, 2002). Biofiltration technology has become quite popular in industries to treat volatile organic compounds (VOC), odors and petroleum hydrocarbons. Additional, similar kinds of pollutants are also being noticed in the indoor environment at alarming levels (Jones, 1999; Wood et al, 2002). Potentially harmful air pollutants may accumulate in enclosed, human occupied systems. VOC's originate indoors from sources like building furnishings, adhesives and cleaning agents (Sheldon et al, 1988). Biological treatment processes have found applications in such indoor environments. B.C. Wolverton's (1990) study showed that

foliage plant system (leaves, potting soil and microbes attached to roots) greatly improves indoor air quality.

Carbon monoxide manifests itself as a formidable outdoor and indoor pollutant. So the development of biofilters to treat CO will have multiple applications. Soil microbes are the second largest sink for CO (Bartholomew and Alexander, 1981; Moxley and Smith, 1998). There are many reports of microorganisms capable of utilizing CO (Nozhevnikova and Yurganov, 1977) and include fungi (Inman and Ingersoll, 1971), algae (Chappelle, 1962), actinomycetes (Bartholomew and Alexander, 1979), carboxydobacteria (Zavarzin and Nozhevnikova, 1977), and CO oxidizing nitrifying bacteria (Conrad, 1996). Also some studies have shown that soil bed reactors (Frye et al, 1992) and foliage plants (Wolverton, 1990) were able to completely and rapidly remove low concentrations (120-130ppm)of CO.

Although biofilters may be proven to eliminate CO emissions or reduce levels, there remains a question as to how environmentally friendly biofilters are compared to other CO control technologies, namely catalytic converters.

1.4 Need for Systems Ecology Based Life-cycle Assessment

The earth and her resources are been continuously diminished on the pretext of increasing economic development. Nature's services are considered free and inexhaustible, with value added only to human services. The concept of industrial ecology has now become important to demonstrate the fact that human economic development and nature have to be balanced. Industrial ecology has been defined by Graedel and Allenby (1995) as "the means by which humanity can deliberately and

rationally approach and maintain a desirable carrying capacity, given continued economic cultural and technological evolution". The principles of industrial ecology focus on making material/product cycles more efficient and designing for the environment (Tilley, 2003). It also advocates 'cradle to cradle' design approach rather than conventional 'cradle to grave' practice.

The life cycle thinking espoused by industrial ecology requires that industries take a lifecycle approach towards subsystems and processes that are a part of its supply chains and sub-chains. It has become imperative to use a life cycle assessment that would incorporate the actual economic gain and environmental impacts of any process or material. Design, manufacturing & operation of environmental pollution control technologies should follow principles of industrial ecology ensuring that the energy and material resources consumed and waste generated are minimized over its entire cycle.

Thus a pollution technology, which very effectively reduces the target contaminant but, indirectly causes a different environmental burden, has to be analyzed for net environmental gain. Therefore, from a systems perspective environmental pollution control strategies should not only ensure that the targeted pollutant is reduced but also that indirect environmental impacts are not created in the process of manufacturing and operating technologies. Integrated system analysis tools should be applied to evaluate environmental technologies to determine their true environmental benefit. Holistic evaluation of integrated ecological-industrial systems requires a methodology that includes systems ecology. The methodology should

realize all the ecological, environmental, social and economic benefits and costs associated with environmental control technologies.

One such system analysis approach is using Emergy Evaluation, which is a scientific method for performing environmental accounting that directly compares environmental and economic inputs on a common basis. Emergy (spelled with an "m") measures both the work of nature and humans in generating a product or service (Odum, 1996). Emergy can be defined as a measure of the total energy of one kind that has already been used in energy transformations directly or indirectly to make a product or service. Different types of energy are compared using the transformity which is defined as emergy per unit available energy. Emergy is a record of energy used and has been called "energy memory". For example, a piece of charcoal has a certain amount of available (potential) energy that is released when it is burnt. It required an even higher amount of energy to make it through many natural processes. Emergy thus makes a distinction between available energy and previously-used available energy that makes it a very powerful tool in system evaluation.

An emergy analysis can be used in any kind of system evaluation especially in environmental systems as it can compare input energies with actual environmental benefit. For example, if we compare two methodologies to treat storm water runoff, a constructed wetland and a heavily engineered filter system, we may find that both may be equally capable to reducing pollutant loads. However the constructed wetland may also add a whole ecosystem, with its complex interactions, giving more value to the technology. An emergy evaluation can consider indirect benefits like these, which give more meaning to an impact assessment study.

1.5 Objectives

My research goals were to quantify the capacity of biofilters to remove CO from air streams and to evaluate the environmental sustainability of biofilters that remove CO. Specifically my study:

1. Determined the CO elimination capacity of biofilters.
2. Determined the effect of media, inoculation, loading and chlorination on removal rate and efficiency.
3. Determined the CO removal efficiency of a biofilter loaded with exhaust from a gasoline powered engine.
4. Compared the environmental sustainability of the biofilter system and compared it to a traditional technology of CO removal.

1.6 Plan of Study

Table 1.1 summarizes the experiments conducted. To determine the CO elimination capacity of biofilters (objective #1), I loaded six bench-scale biofilters with CO and measured the inlet and outlet concentration.

Objective # 2 was achieved by measuring the performance of two different media, compost and pebbles, inoculating the biofilters with slurries made from local soils, loading the biofilters with bottled CO at either 100 ppm or 1000 ppm and dosing a biofilter with hypochlorite.

Table 1.1 Preview of experiments			
Objective #	**Experiment**	**Data Collected**	**Analysis**
1, 2	**Batch/Bottle** Fill-wait-read outlet CO. Source: Bottled CO	Record start + end CO concentrations.	t-test Non linear least squares model Univariate ANOVA
1, 2	**Continuous/Bottle** Continuously supply CO- Continuously read outlet. Source: Bottled CO	Record outlet CO concentrations.	Time series
2, 3	**Continuous/Engine** Continuously supply Engine exhaust Read inlet and outlet. Source: Engine exhaust CO	Record inlet CO concentrations at intervals and outlet CO at all other times.	Time series Univariate ANOVA
2	**Continuous/Bottle with chlorination** Continuously supply CO- Chlorinate media- Observe effects of chlorination on removal.	Record outlet CO concentrations	Time series
4	**Environmental Accounting** Compare lab-scale and pilot-scale biofilter to traditional catalytic converter technology	Calculate environment and economic resource inputs and CO removed	Emergy evaluation

To meet objective # 3, I fed 4 biofilters 700 ppm or 1000 ppm CO generated in the exhaust of an internal combustion engine.

Objective # 4 involved performing emergy evaluation of the lab-scale biofilter, a modeled pilot-scale biofilter operating under industrial conditions and a traditional automotive catalytic converter.

Chapter 2: Material and Methods

This chapter is divided into two main topics: Section 2.1 describes the biofilter lab experiments. Section 2.2 describes the emergy evaluation method used to perform the environmental accounting of the biofiltration technologies.

2.1 CO Biofiltration

2.1.1 Description of system

Previously used designs for bench scale biofilter units (Jones et al, 2002) were built in the University of Maryland Biological Resources Engineering (UMBRE) Project Development Center (College Park, MD). Six cylindrical biofilters, 15 cm in diameter and 1 m in height were constructed of clear PVC (Figure 2.1). Each biofilter had a bottom port and two top ports for sampling CO. Lids with fitted clamps and rubber sealers were provided to close both ends of each biofilter. A thin plastic grid was placed in each biofilter at a height of 15 cm from the bottom of the PVC pipe, to support biofilter media and allow for drainage. The bottom lid was also fitted with a port for leachate drainage and collection. A safety valve was also fitted on the bottom lid. Non-reactive and non-absorbing Tygon® tubing (US Plastic Corp., Lima, OH) was used for all gas transport. The six biofilters were mounted upright on a steel and wooden frame, built at the UM BRE Project Development Center.

Figure 2.1: Biofilter setup in the laboratory

Three PVC cylinders were filled with inert, hardened baked clay "pebbles" (Grorox®, Home Harvest® Garden Supply Inc., Baltimore, MD) with diameters of 8-16 mm. The three pebble biofilters were designated #'s 1, 3 and 5. The remaining three PVC cylinders were filled with poultry litter compost generated at the composting facility at the University of Maryland's Lower Eastern Shore Research and Education Center (Poplar Hill, MD). The three compost biofilters were designated #'s 2, 4 and 6. The biofilters were irrigated with de-chlorinated water to

maintain a moist environment. The biofilters were inoculated with slurries made from soils located on the University of Maryland campus (College Park, MD). Soil innoculum was made by collecting cylindrical soil cores (5 x 5 cm) from forests and wetland sites. The soil was sieved (ASTM sieve No.40) and mixed with one liter of dechlorinated water to form slurry. Nutrient additions in the form of 20 ml of 0-5-4 solution (N-P-K solution, Flora Bloom ®, General Hydroponics®,

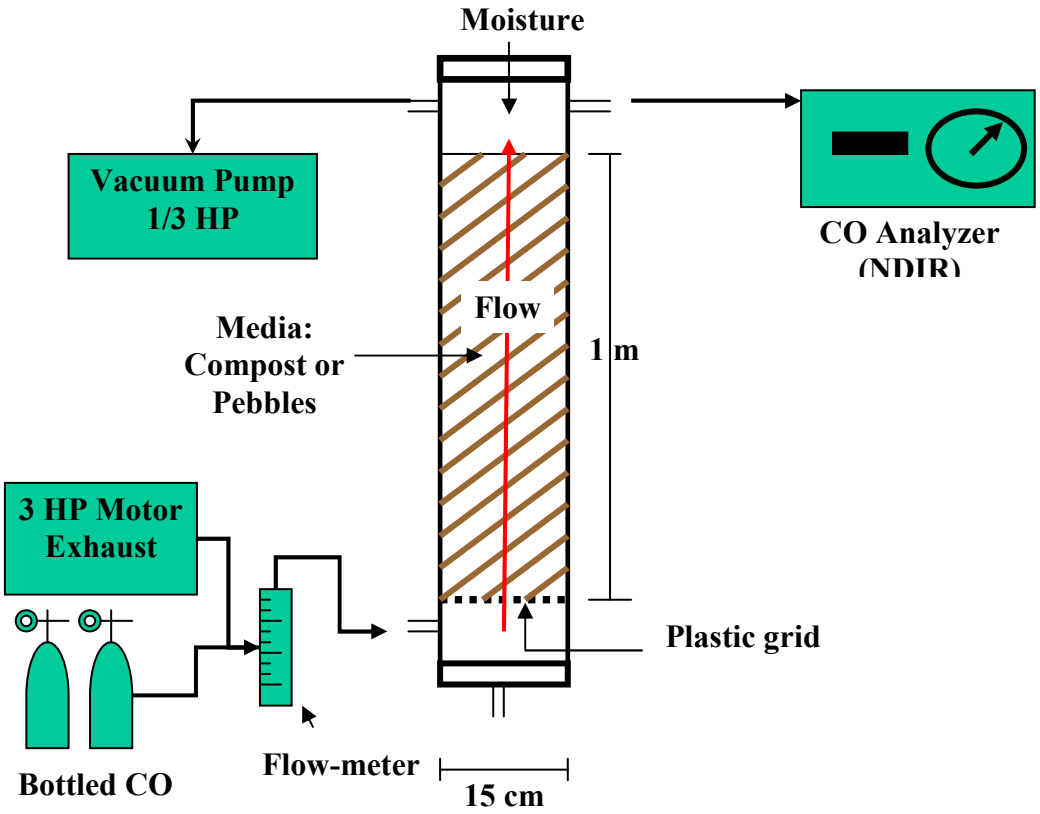


Figure 2.2: Biofilter Flow Diagram

Sebastopol, CA) and 20 ml of 5-0-1 solution (N-P-K solution, Flora Micro®, General Hydroponics®, Sebastopol, CA) were added to the soil slurry. This soil innoculum was added to the compost and pebble biofilters through the top lid.

CO contaminated air was pulled through the units from the bottom and measured for reduction in CO concentration upon exit from the top of the PVC cylinders. Two sources of CO were used to test the biofilters. One was bottled CO (Airgas East, Salem, NH) at a known concentration mixed with air. The other CO source was a gasoline engine exhaust containing CO mixed with other combustion products. CO-containing exhaust was generated by a 2,620 W (3.5 HP) four-stroke gasoline engine (Briggs and Stratton, Corp., USA). A 250 W (1/3 HP) vacuum pump (High Vacuum Pump, Model: E2M 2, Franklin Electric, Bluffton, IN), attached to one of the top ports of each biofilter, pulled exhaust gas containing CO through the biofilter media from the bottom (Figure 2.1).

CO concentrations were measured with a Non-Dispersive Infrared (NDIR) gas analyzer (Model 200, California Analytical Instruments (CAI), Orange, C Inlet CO to bottom port of BF outlet readings from the gas analyzer were continuously logged using a da (HOBO® Outdoor 4-Channel data logger, Onset Computers, Cape Cod, M flow rates were measured and controlled with stainless-steel flow meters (Gilmont Inc., Barrington, IL) at the biofilter inlet.

2.1.2 Data Collection

CO elimination capacities of the biofilters were studied under two different flow conditions: batch flow and continuous flow conditions.

Batch/Bottle: Figure 2.3 shows a top view of the biofilter experimental setup for the batch flow experiments. In the batch experiments, bottled CO at 1000 ppm was pumped into the biofilter until CO concentration at the top port reached steady state value of close to 1000ppm-CO. This was the Start concentration. The biofilter

ports were then closed. All six biofilters were exposed to the CO for the same prescribed period, at the end of which End concentrations were sampled from the top port.

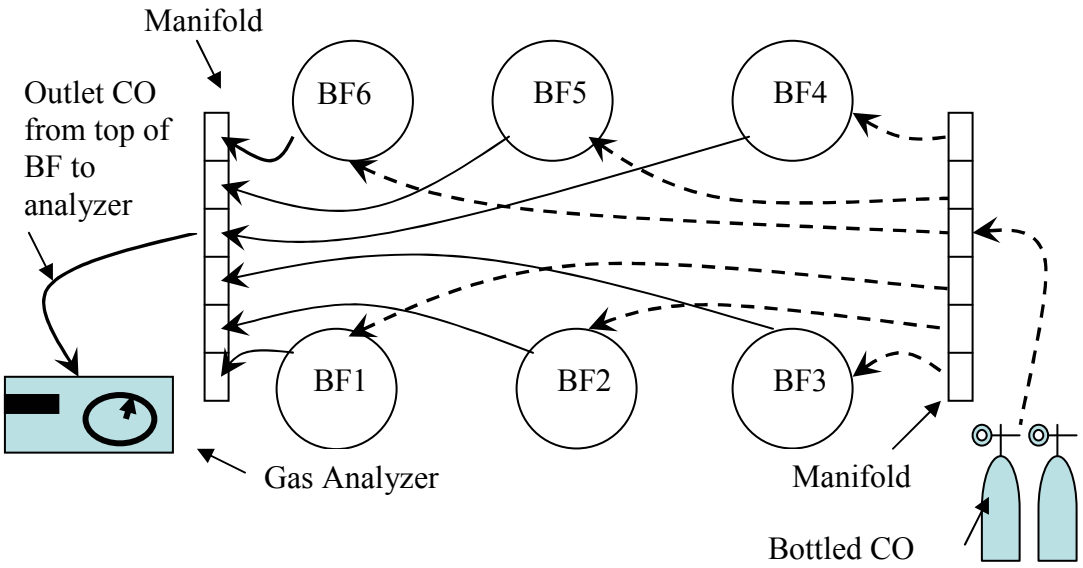


Figure 2.3: Top view schematic of the batch/bottle experimental setup

The Start and End CO concentrations displayed by the NDIR CO analyzer were noted and recorded manually in a laboratory notebook. Batch experiments were carried out on the six biofilters for 60 days, with the all the biofilters being exposed to the same prescribed number of hours on any day. The biofilters were exposed to anywhere between 2 to 90 hours before End concentrations were sampled. Table 2.1 shows a timeline of the batch experiments with biofilter exposure time.

In the continuous flow experiments the pollutant CO air stream was continuously passed through the biofilter. Real time outlet CO concentrations from the analyzer were logged using the data logger. These continuous flow studies were carried out using bottled CO and CO engine exhaust as the input CO pollutant stream.

Table 2.1: Timeline of batch/bottle experiment (hours of exposure)

	Day1	Day1.5	Day2	Day2.5	Day3	Day3.5	Day4	Day5	Day6	Day7	Day7.5	Day8	Day9
Compost	5.25	17.75	4.25	18	3	67	0	0	0	5	17	0	23.75
Pebble	0	0	0	0	0	0	0	0	0	0	0	0	23.75

	Day10	Day11	Day12	Day13	Day14	Day15	Day16	Day17	Day18	Day19	Day20	Day21	Day22
Compost	21.25	94	0	0	0	22.5	6.25	25.5	0	0	0	0	0
Pebble	21.25	94	0	0	0	22.5	6.25	25.5	0	0	0	0	0

	Day23	Day24	Day25	Day26	Day27	Day28	Day28.5	Day29	Day30	Day31	Day32	Day33	Day34
Compost	0	0	0	0	0	2.5	20	2.5	0	19	68	0	0
Pebble	0	0	0	0	0	2.5	20	2.5	0	19	68	0	0

	Day35	Day36	Day36.5	Day37	Day38	Day39	Day40	Day41	Day42	Day43	Day44	Day45	Day46
Compost	6	4.5	16	8	0	0	0	0	0	0	4.5	4.5	4
Pebble	6	4.5	16	8	0	0	0	0	0	0	4.5	4.5	4

	Day47	Day48	Day49	Day50	Day51	Day52	Day53	Day54	Day55	Day56	Day57	Day58	Day59
Compost	0	0	4.5	0	0	0	0	5	5.5	7	4	5	4
Pebble	0	0	4.5	0	0	0	0	5	5.5	7	4	5	4

	Day60
Compost	7.5
Pebble	7.5

Continuous/Bottle: Figure 2.4 shows the experimental setup for the continuous/bottle experiments. Bottled CO containing 1008 ppm CO mixed with air was pulled through the compost biofilter (#6) by the vacuum pump for 6 hours during any run.

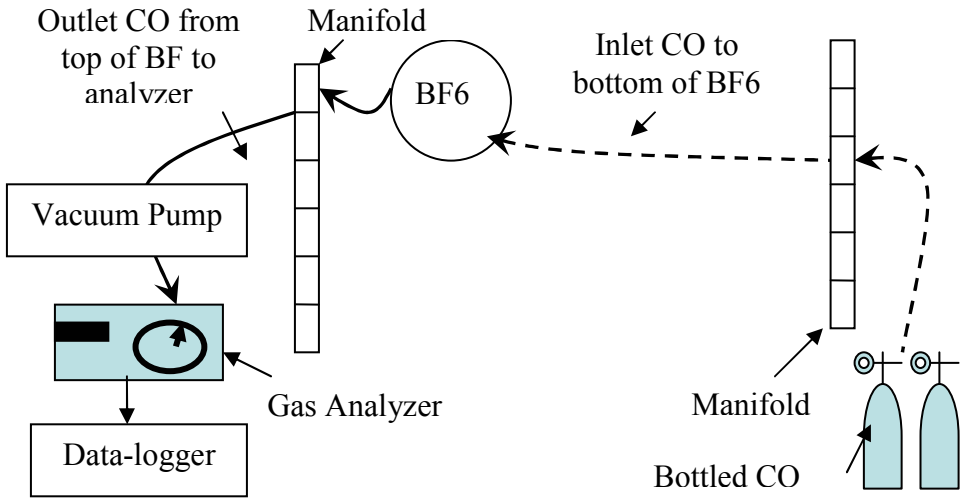


Figure 2.4: Top view schematic of the continuous/bottle experimental setup

CO flow through the biofilter and the vacuum pump was maintained and controlled at 0.5 liters per minute (l/min). The outlet CO concentration from the top port of biofilter #6, read by the CO analyzer was logged every 2 seconds using the HOBO data-logger. The steady state CO concentration at the outlet was noted at the end of each run. The biofilter was run for 78 days, was inoculated with soil slurries on some days and left idle (not run) on other days. The effects of these treatments on the dynamics of the biofilter outlet concentration were studied over time. The biofilter was inoculated with one liter soil and nutrient slurries on Day 5 and Day 25. The compost biofilter was also put on "idle" from Day 35 to Day 70, after which it was run as previously to study the effect of idling on the natural biofilter mechanism.

Continuous/ Engine: Figure 2.5 is a top view of the experimental setup for the continuous/engine experimentation on the biofilters.

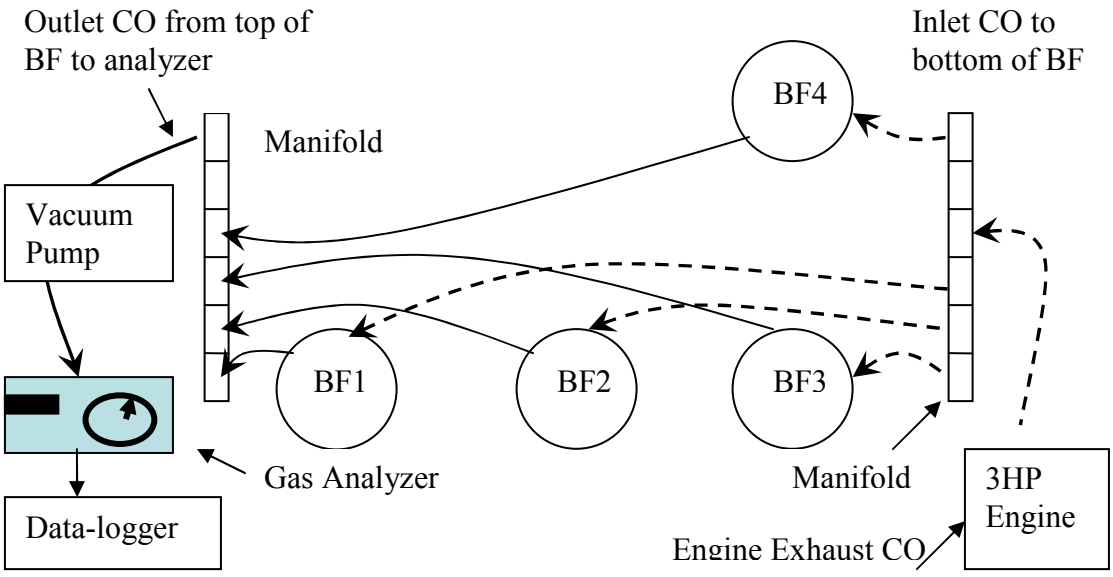


Figure 2.5: Top view schematic of the continuous/engine experimental setup

To study the removal efficiency of engine exhaust-CO, CO-containing exhaust from the 3.5 HP engine was continuously fed into two compost biofilters and two pebble biofilters. The two compost biofilters were called CM2 and CM4, the pebble biofilters were called PM1 and PM3. These biofilters are named differently than the ones that underwent bottled CO treatment, as a new stock of compost and pebble media (but from original batch) was used for the bottled CO experiments. The vacuum pump pulled the CO-exhaust through the biofilters through tubing stationed near the mouth of exhaust outlet of the engine. One compost (CM4) and one pebble biofilter (PM1) were fed engine exhaust with approximately 700 ppm CO concentration, while the others (CM2 and PM3) were fed engine exhaust at approximately 1000 ppm-CO. The two different levels of CO exhaust (~ 700 ppm and ~1000 ppm) were obtained by adjusting the point of uptake from engine exhaust. The

biofilters operated on two 4-hour cycles per day, which were approximately from 9:00 am to 1:00 pm and 2:00 pm to 6:00 pm. This constituted a "test". The vacuum pump was used to pull the contaminant air through the media and maintain 1.2 l/min flow-through conditions. Since the CO analyzer could only measure a single air stream at a given time, the biofilter inlet (engine exhaust) was read every 30 minutes for 3 minutes, while the biofilter outlet was read at all other times. Four "tests" were carried out on each biofilter (CM1, CM2, PM1 and PM2). Two runs were carried out without any inoculation and two runs were carried out after inoculation with local soil slurries.

To confirm the microbial uptake of CO through biofilter media one compost biofilter (#6) was treated with hypochlorite to test whether microbial activity was responsible for CO removal. A test involved passing bottled CO at 100 ppm through the biofilter for about 3 hours per day. These tests were carried out on 5 days in a span of 22 days prior to chlorination. The outlet concentration was continuously logged every 2 seconds and steady state CO ppm for each day was recorded. The compost biofilter (#6) was disinfected on Day 22 of the chlorination experiment. Hypochlorite (HOCl) solution was mixed as would be done to disinfect water for drinking purposes at home (Water disinfection, online report, 2004). A 6% HOCl solution (Clorox Ultra 6%, Oakland, CA) was mixed with 5 parts of dechlorinated water to form a 1% HOCl solution. Five (5) ml of this 1% solution was then mixed with 19 liters (5 gallons) of dechlorinated water. One liter of this prepared chlorine solution was added to the compost biofilter. Three runs were carried out on the biofilter after the HOCl treatment to measure the CO removal rate. The effect of

HOCl disinfection on biofilter CO removal was evaluated by comparing the before and after removal rates.

2.1.3 Data Analysis of Biofilter Performance

Batch/Bottle: To assess the performance of the biofilters under batch flow conditions, the start and end CO concentrations were used to compute the removal efficiency.

$$\text{Removal efficiency under batch flow } (R_B) = \frac{\text{Start CO Concentration } (ppm) - \text{End CO Concentration } (ppm)}{\text{Start CO Concentration } (ppm)} \qquad 2.1$$

The removal efficiency for the biofilters calculated according to equation 2.1 was grouped under exposure times of 2-4 hours, 4-6 hours, 6-8 hours, 8-24 hours and >24 hours. All observations for each exposure group with three replicates for each media were considered to calculate average removal for both media under each exposure group. The removal efficiencies for the compost and pebble media were compared with a t-test on the means at a 5% level of significance.

The CO degradation in the biofilter during batch treatment was assumed to be first order, and can be represented by Equation 2.2:

$$C_o = C_i e^{kE_t} \qquad 2.2$$

where

C_o = Outlet CO concentration (ppm) from biofilter

C_i = Inlet CO concentration (ppm) to biofilter

k = 1st order rate constant

E_t = Exposure time for that run

Therefore 1st order rate constant can be calculated as:

$$k = -\frac{\ln[C_o / C_i]}{t} \qquad 2.3$$

The 1st order rate constant for each of the three replicates of each media was computed according to equation 2.3 and an average k-value for each media type was determined. Difference in k between the compost and pebble media was compared using a t-test on the means at a 5% level of significance.

The removal efficiency of the biofilter improved as it operated repeatedly. The number of days that the biofilter has been operated with the existing conditions contributed to its maturity and this time (days) was called 'Maturity Time, M_t'. To see the effect of exposure time (E_t) and maturity time (M_t) on the biofilter, I developed a model using data from all six biofilters. A non-linear model was developed using a non-linear least squares methodology described by McCuen and Snyder (1986). This method requires: an objective function, a model, a data set and an initial set of estimates for the unknowns.

We know that the CO removal efficiency (R_B) of the biofilter under batch conditions depends on E_t and M_t. Therefore the removal efficiency in the objective function can be defined as

$R_M = f(E_t, M_t, A, B)$, where A and B are model coefficients and R_M is removal efficiency.

Biofilter CO removal efficiency is assumed to increase exponentially with exposure time and maturity time before reaching steady state removal. Also, at time = 0, (i.e. before any exposure to pollutant) removal is 0. Through these basic characteristics of my data, viewing sample models and through discussions with R.H. McCuen (personal communication), I decided to use an exponential growth model to fit my data set. The general exponential model was in the form of $y = 1 - e^{-kx}$. Since the batch flow model of CO removal efficiency was dependent on exposure time (E_t) and maturity time (M_t), I altered the model to reflect these two parameters as follows.

$$\text{Removal efficiency of model } (R_M) = 100\,(1 - e^{-(AM_t{}^B)E_t}) \qquad 2.4$$

The value of removal efficiency is specified by two variables E_t and M_t and two coefficients: A and B. The basic approach to non-linear solutions is based on Taylor series expansion of models to be fitted. This method of fitting coefficients based on Taylor's series is explained in detail in Appendix B. The coefficients for biofilters #1, #2, #3 and #4 were found using a FORTRAN computer program developed by McCuen (1993) that used the least squares method. The model calibration on the compost biofilters was carried out on compost #2 and 4 by plotting the measured versus predicted CO removal efficiencies. The correlation coefficient and standard error of estimate was computed for these calibrated models. Model validation was performed in the following way: Coefficients obtained for the compost model #2 and #4 were averaged to obtain new model coefficients. The predicted removal efficiencies from this model were validated against observed removal efficiencies of compost #6. Correlation coefficient and standard error of estimate were calculated for

the validated model. Similarly for pebble biofilters, model calibration was carried out on pebble biofilter #1 and #3 and validation was carried out on pebble biofilter #5.

A combined model was also developed for the compost biofilters, which included data from all three compost biofilters. Similarly, a combined model was also developed for the pebble media. The coefficient of correlation (r) between the predicted and observed data and the standard error of estimate (S_e) for the predicted values was computed. The behavior of the models to increasing exposure time Et (to about 100 hours) at a constant maturity time was studied and compared between both media. Also, the response of the model to a constant exposure time of 8 hours, matured over a hundred days was plotted and results for both media were visually compared.

Continuous/Bottle: For the continuous CO flow, removal efficiency (R_C) was calculated for each run as follows.

$$\text{Removal efficiency under continuous flow } (R_C) = \frac{\text{Inlet CO Concentration } (ppm) - \text{Outlet CO Concentration } (ppm)}{\text{Inlet CO Concentration } (ppm)} \qquad 2.5$$

For the continuous flow experiments using bottled CO, the inlet concentration was constant at 1008 ppm. The outlet CO concentration from compost biofilter #6, recorded by the logger was used to calculate the mass uptake. Using this constant inlet concentration (I), outlet concentration (O) and flow rate (F.R.) of 0.5 l/min, CO budget was calculated. Density of air was taken as 1.23 mg/cm^3. The mass inflow and outflow were calculated according to Equations (2.6) and (2.7).

CO mass inflow (mg/min) = $I \frac{cm^3}{m^3} \times F.R. \frac{L}{\min} \times 0.001 \frac{m^3}{L} \times 1.23 \frac{mg}{cm^3}$ 2.6

CO mass outflow (mg/min) = $O \frac{cm^3}{m^3} \times F.R. \frac{L}{\min} \times 0.001 \frac{m^3}{L} \times 1.23 \frac{mg}{cm^3}$ 2.7

The CO budget for the biofilter can be expressed as:

Uptake by the biofilter (mg/min) = CO mass inflow (mg/min) – CO mass outflow mass (mg/min) 2.8

Continuous/Engine: For the continuous flow experiments through the biofilters with CO engine exhausts, CO produced by the engine exhaust was observed to be highly variable in concentration. Hence the outlet CO concentration from the biofilter was also variable. To calculate R_C in Equation 2.5, I averaged the inlet and outlet CO concentration over time of the run. The CO mass uptake was calculated using Equations 2.6, 2.7 and 2.8 using this average inlet concentration (I), average outlet concentration (O) and flow rate (F.R.) of 1.2 l/min. Density of air was taken as 1.23 mg/cm^3. A mixed effects 3-factor ANOVA determined the significance of the effect of media, inlet concentration (loading) and inoculation.

Continuous/Bottle with chlorination: The chlorination experiment was conducted as a continuous flow experiment with CO provided by a bottle on a single compost biofilter (#6). Equation 2.5 was used to calculate removal efficiency. Outlet concentration was determined from the steady state of each day's experiment. The effect of chlorination on biofilter performance was evaluated by comparing the removal efficiency before and after dosing with HOCl.

2.2 Environmental Accounting

My objective in this thesis was to compare the environmental resource requirements of three technologies that can remove CO from air streams (a lab-based biofilter, a pilot-scale biofilter and a platinum-based catalytic converter). We performed a standard emergy evaluation to determine the solar emergy required to construct and operate each technology over its estimated lifetime. Emergy is the available energy of one kind previously used up directly or indirectly to make a service or a product. Its unit is the emjoule (Odum, 1996). When all energies are expressed in terms of solar energy, the resulting emergy is called solar emergy and is represented by sej (solar emjoule).

I compared the CO-compost biofilter system emergy requirements to that of a more conventional CO treating technology, the catalytic converter. To make an accurate and fair comparison, I scaled up my laboratory compost biofilter system to a pilot-scale model and then compared it to the technologically advanced catalytic converter. Since emergy measures both the work of nature and humans required to generate products and services (Odum, 1996) it is able to compare environmental and economic values which helps in sound decision making on environmental issues.

2.2.1 Emergy Methodology

The product or service to be analyzed is considered to be a system with well defined boundaries. Therefore the boundary conditions of the lab-scale biofiltration setup, pilot-scale biofiltration setup and the catalytic converter system are defined and the various energy inputs and outputs to this system over a 10 year-life time are

identified. To make an accurate representation of the system, an energy diagram of the system is developed, called the *Energy Systems Diagram.* The energy systems diagram was developed for a generic compost biofilter (lab-scale and pilot) and the catalytic converter. Based on the energy systems diagrams, an emergy evaluation table was developed to calculate emergy values (Table 2.1).

Input items in the emergy table can be either in units of energy, mass or money, which are transformed to solar emergy using Equations 2.9, 2.10 and 2.11 respectively.

$$Energy\ Transformation\ Ratio\ (ETR) = \frac{Emergy\ (sej)}{energy\ (J)} \quad 2.9$$

$$Mass\ Transformation\ Ratio\ (MTR) = \frac{Emergy\ (sej)}{gram\ (g)} \quad 2.10$$

$$Dollar\ Transformation\ Ratio\ (DTR) = \frac{Emergy\ (sej)}{money\ (\$)} \quad 2.11$$

The solar emergy of all items were summed to find the total solar emergy driving the system. Total Emergy of a system (TE) can be mathematically represented as

$$TE = \sum_{i=1}^{n} ETR \cdot e_i + \sum_{j=1}^{p} MTR \cdot m_j + \sum_{k=1}^{q} DTR \cdot d_k \quad 2.12$$

e_i – energy of input *i*

m_j – mass of input *j*

d_k – dollars of input *k*

To compare the resource intensity of the three CO treatment technologies the solar emergy per gram of CO removed was calculated using Equation 2.13.

$$Emergy\ per\ gram\ of\ CO\ removed = \frac{Total\ Emergy\ of\ the\ system(TE)}{CO\ removed\ (g)\ over\ 10\ year\ life} \qquad 2.13$$

Table 2.2: Template for identifying and quantifying resource inputs and outputs in an Emergy Analysis.

1 *Note*	2 *Item*	3 *Data*	4 *Units*	5 *Transformity (sej/unit)*	6 *Solar Emergy (sej/yr)*
1.	Electricity	e_i	joules	ETR_i	ETR x e_i
2.	Steel	m_j	grams	MTR_j	MTR x m_j
3.	Services	d_k	$	DTR_k	DTR x d_k

2.2.2 Laboratory Biofilter System

Emergy evaluation of the lab-scale biofilter involved two parts. First the total emergy required to build, operate and maintain the lab-biofilters was calculated (Equation 2.12). Next the CO uptake by the biofilter over its 10 year life was estimated.

The solar emergy of compost media, construction materials, labor and electricity to build and operate the lab-biofilters were calculated for an expected life of 10 years or 2,080 hours (5 day/week, 8 hour/day) of operation per year. The media was assumed to last three years while other material components were assumed to last 10 years. Transformation ratios were adopted from Odum and Brown (1993) Odum (1996), and Buranakarn (1998).

To calculate CO budget for the lab-scale biofilter, the engine exhaust with ~ 1000 ppm CO was run through the biofilter and outlet CO concentration was measured at the top port continuously for about 7 hours. The variable CO inlet

concentration level from the engine exhaust was averaged to obtain an inlet CO concentration for the run. Similarly the outlet CO concentration was obtained. Using equations 2.6, 2.7, and 2.8, the CO uptake (mg/hr) was calculated.

2.2.3 Pilot Scale Biofilter

To evaluate the emergy needs of a commercial, CO-treating biofilter, I scaled up our lab-scale biofilter to a pilot model and assumed the operational characteristics of a biofilter sold by Biofiltration Inc., of Northridge, CA (DeVinney, 1999). The emergy analysis assumed a 10-year operational life for the biofilter. The pilot scale model treated 17,000 m^3/hr of CO gaseous stream and operated 2,080 hours a year (5 day/week, 8 hour/day). It contained 314 m^3 of compost media with a 3-year life and empty-bed contact time (EBCT) of 70 seconds. The pilot model had a $550,000 installation cost and a $0.83 per 1000 m^3 maintenance cost associated with operation. The biofilter included a 30 KW (40HP) centrifugal blower and treated CO at the same removal rate per unit of media volume as the lab-scale system (0.53 mg/min by 0.0121 m^3 of media), which equals 43.8 mg-CO m^{-3}-media min^{-1} or 13.8 g-CO min^{-1} for pilot biofilter

2.2.4 Catalytic Converter

Typical catalytic converters treat an inlet CO concentration of about 4,800 ppm (Poulopoulos and Philippopoulos, 2000). The catalytic converter assessed for the emergy analysis consisted of five essential components as described by Corning Inc. (2001):

- *Substrate:* A ceramic honeycomb-like structure that provides a large surface area for the application of washcoat and precious-metal catalyst that renders the compounds of engine exhaust to harmless components.
- *Insulation Mat:* A wrapping around the catalyzed substrate that provides thermal insulation and protects against mechanical shock.
- *Can:* A steel package that encases the catalyzed substrate and mat, and integrates it into the exhaust system.
- *Washcoat:* A coating that increases the surface area of the substrate for catalysis.
- *Catalysts:* Catalytically active precious metals like platinum, palladium and rhodium are incorporated into the washcoat. The treated washcoat is then applied to the ceramic substrate.

The total emergy values for all the above components of the catalytic converter were calculated from Equation 2.12. Detailed calculations for the CO budget of the catalytic converter are given in the Appendix C. Using the total emergy of the system and the CO uptake over its 10-year life, the emergy/g-CO removed was calculated from Equation 2.13.

2.2.5 Modeled Performance of Catalytic Converter at Lower CO levels

Since a catalytic converters operates at a much higher CO concentration (4800 ppm) than the CO concentration of my biofilter (1000 ppm), it was necessary to estimate how well the catalytic converter would perform under lower concentrations. I developed a simple model that predicted CO removal of the catalytic converter at lower concentrations. I assumed that the catalytic converter operated at lower inlet

CO concentrations would require the same emergy inputs. The developed model predicted CO removal rate of the catalytic converter operated at inlet concentrations of 5, 50, 500, and 5,000 ppm-CO.

$$R_{cc} = k_2 C_i^2 Q \qquad 2.13$$

C_i = CO concentration at inlet to catalytic converter mg/m^3

Q = flow rate m^3/s

k_2= 2^{nd} order rate constant

Thus, the catalytic converter removes more CO if inlet CO concentration is higher. This relation can be used to make a more accurate comparison of the catalytic converter to the biofilters as the catalytic converter treats CO in the range of 4800 ppm, while the lab-scale and pilot scale model treated CO around 1000 ppm.

The total emergy requirement of the catalytic converter (TE_{cc}), according to Equation 2.14 is given by:

$$TE_{cc} = \sum_{i=1}^{n} ETR \cdot e_i + \sum_{j=1}^{p} MTR \cdot m_j + \sum_{k=1}^{q} DTR \cdot d_k$$

$$\text{Therefore } \frac{Emergy\ of\ catalytic\ converter}{CO\ removed} = \frac{TE_{cc}}{R_{cc}} \qquad 2.14$$

The total emergy used per gram of CO treated was calculated for the three technologies and plotted against respective CO exposure levels to clearly compare the CO removal efficiencies.

Chapter 3: Results

The results section is divided into two sections. Section 3.1 details the performance of the compost and pebble biofilters in removing carbon monoxide and section 3.2 reports on the CO emergy evaluation of the biofiltration technology.

3.1 Performance of Biofilters for CO Removal

3.1.1 CO Removal Performance of Biofilters under Batch Loading

The mean CO removal efficiencies of the compost and pebble biofilters and the significance of their difference are given in (Table 3.1). In general, the compost biofilter exhibited higher removal efficiencies than the pebble biofilter except for the >= 24 hour exposure time but the difference was only significant for the 6-8 hr and 8-24 hour exposure times ($p < 0.05$) (Table 3.1).

Figure 3.1 shows a graphical representation of the removal efficiencies and the computed standard error of estimate for the compost and pebble biofilter for the different exposure times. CO removal efficiencies approached 100% for each media type and increased as exposure time increased but rate of increase in removal efficiencies declined as exposure time increased.

Table 3.1: Removal efficiencies of compost and pebble media under batch flow conditions

Exposure time for batch removal	Mean Removal Efficiency (%)		p-value	No. Samples
	Compost	Pebble		
2 – 4 hrs	38.0	35.6	0.368	15
4 – 6 hrs	56.5	51.7	0.120	72
6 – 8 hrs*	79.6	64.9	0.003	21
8 – 24 hrs*	88.5	81.6	0.008	51
> 24	92.1	96.2	0.100	21

*- significantly different at $\alpha = 0.05$

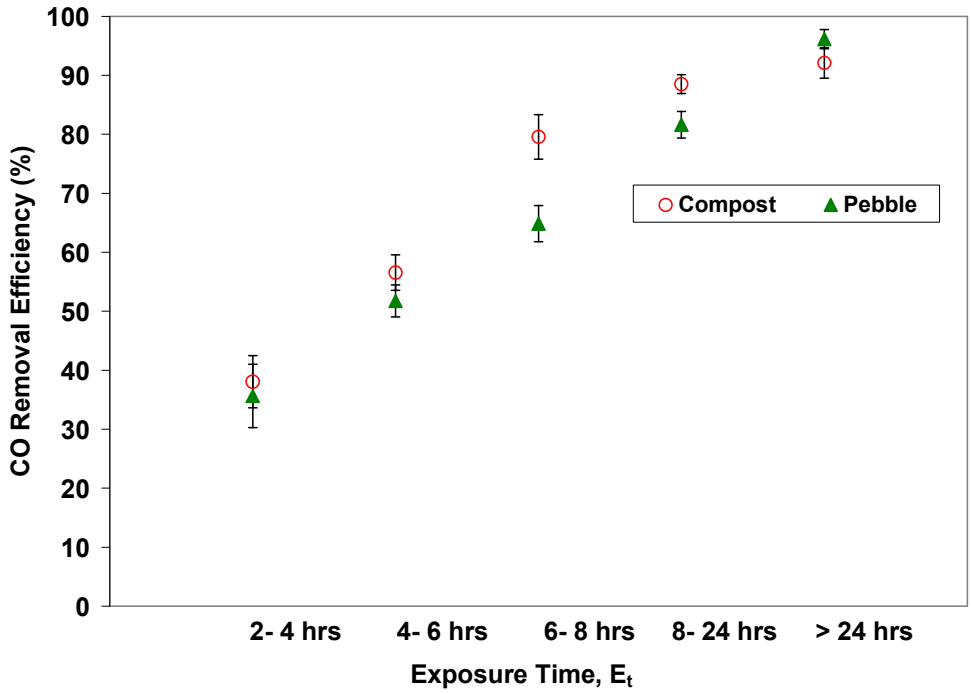


Figure 3.1: Comparative performance of the compost and pebble biofilter at different exposure times with the standard error for each.

The 1st order rate constant of CO uptake (k), computed with Equations 2.2 and 2.3 is given in Table 3.2. The compost biofilter showed a higher rate constant than the pebble biofilter for all the exposure times but was significantly higher only for the 6-8 hours and 8-24 hours exposure times only ($p < 0.05$).

Table 3.2: 1st order rate constant of CO uptake for compost and pebble media under batch flow conditions

Exposure for batch removal	1st order rate constant, k		p-value
	Compost	Pebble	
2 – 4 hrs	0.183	0.151	0.303
4 – 6 hrs	0.211	0.179	0.212
6 – 8 hrs*	0.290	0.157	0.043
8 – 24 hrs*	0.141	0.100	0.010
> 24	0.072	0.071	0.468

*- significantly different at $\alpha = 0.05$

Model parameters for each of the six biofilters were developed using non-linear least squares method (Table 3.3). The calibrated compost biofilters, #2 and #4 showed a correlation coefficient (r) of 0.7454 and 0.9053 respectively between the predicted and observed removal efficiencies. The standard error of estimate for compost #2 and #4 was calculated as 15.667 % and 10.352% respectively. The coefficients obtained for validation of compost BF #6 (average of compost #2 and compost #4 coefficients) are given in Table 3.3. These coefficients predicted removal efficiencies for compost #6 with an r value of 0.8198. The standard error for the validated model was computed as 13.215. The calibrated pebble biofilters, #1 and #3 showed an r value of 0.6924 and 0.9634 with standard error of estimate being 16.891% and 5.365% respectively. The model coefficients for validating pebble BF #5, obtained by averaging coefficients for pebble #1 and #3 are shown in Table 3.3. The predicted removal efficiencies for pebble # 5 showed an r value of 0.9655 with the observed removal efficiencies for #5, thus showing a standard error of estimate of 9.727%.

Figure 3.2a shows the model calibration for the compost models # 2 and # 4. The measured and predicted values for compost biofilter # 2 and compost biofilter # 4

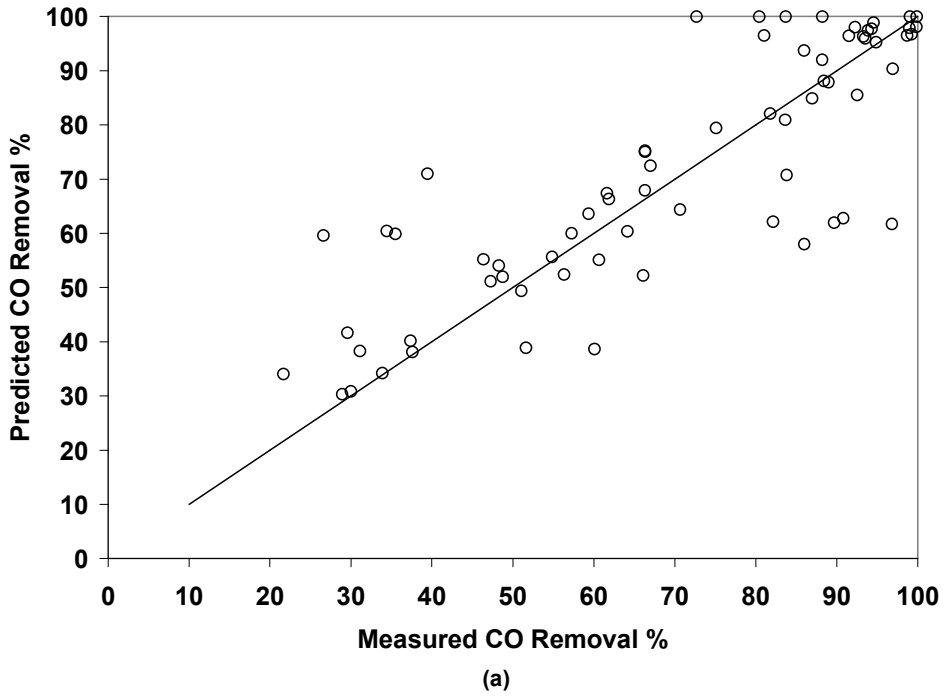
were plotted with the zero error line to visually compare the accuracy of prediction. The data spread appears uniformly distributed about the zero-error line, without any apparent bias. Figure 3.2b is the plot to validate the compost biofilter #6. The model for compost #6 was validated by plotting the measured data from compost # 6 versus predicted values from the model and compared to the zero error line. The data appears to be well spread about the zero error line, indicating no model bias.

Table 3.3: Model Parameters for CO Batch Flow

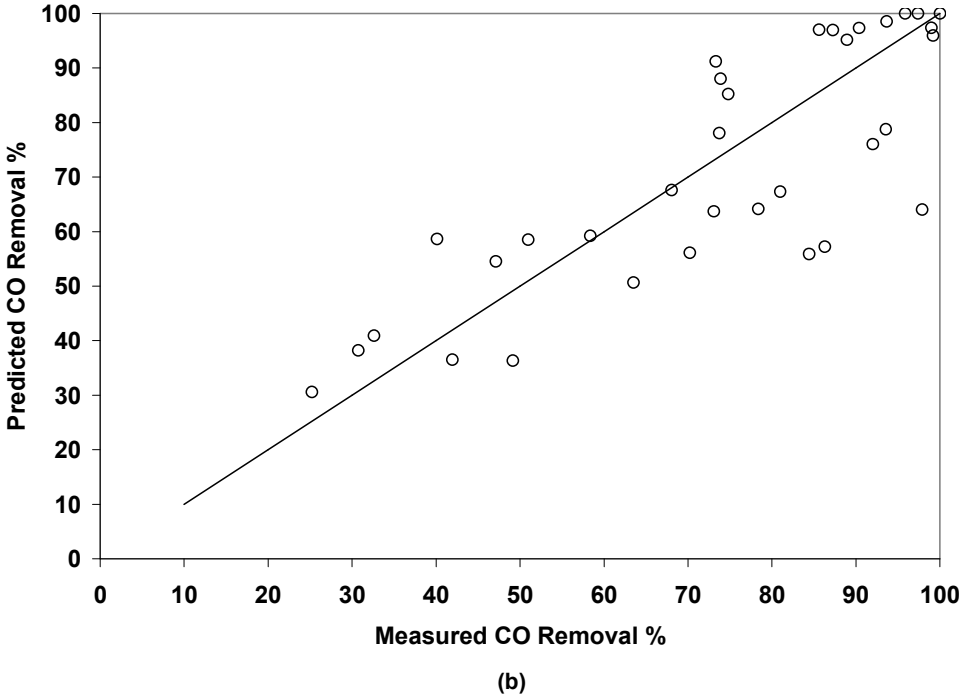
Model: Removal Efficiency $= 100\,(1 - e^{-(A\,M_t^{\,B})E_t})$

Model Description	Coefficient A	Coefficient B	r	Standard Error (S_e) for Removal Efficiency (%)	Comments
Model Calibration					
Compost 2	0.0979	0.2078	0.7454	15.667	Calibrated
Compost 4	0.1027	0.0145	0.9053	10.352	Calibrated
Pebble 1	0.0251	0.4863	0.6924	16.891	Calibrated
Pebble 3	0.0321	0.4500	0.9634	5.365	Calibrated
Model Validation					
Compost 6	0.1003	0.1111	0.8198	13.215	Validated
Pebble 5	0.0286	0.4682	0.9655	9.727	Validated

Figure 3.3a is a plot of model calibration for the pebble media, using data from pebble biofilters # 1 and # 3. The spread of data is even and no bias is evident between the predicted and measured values. Figure 3.3b presents the validation of the pebble model. The data seems to be slightly skewed, toward the top of the zero error line, indicating some bias or over prediction. Models for pebble #1 and #3 seem to over predict for pebble #5

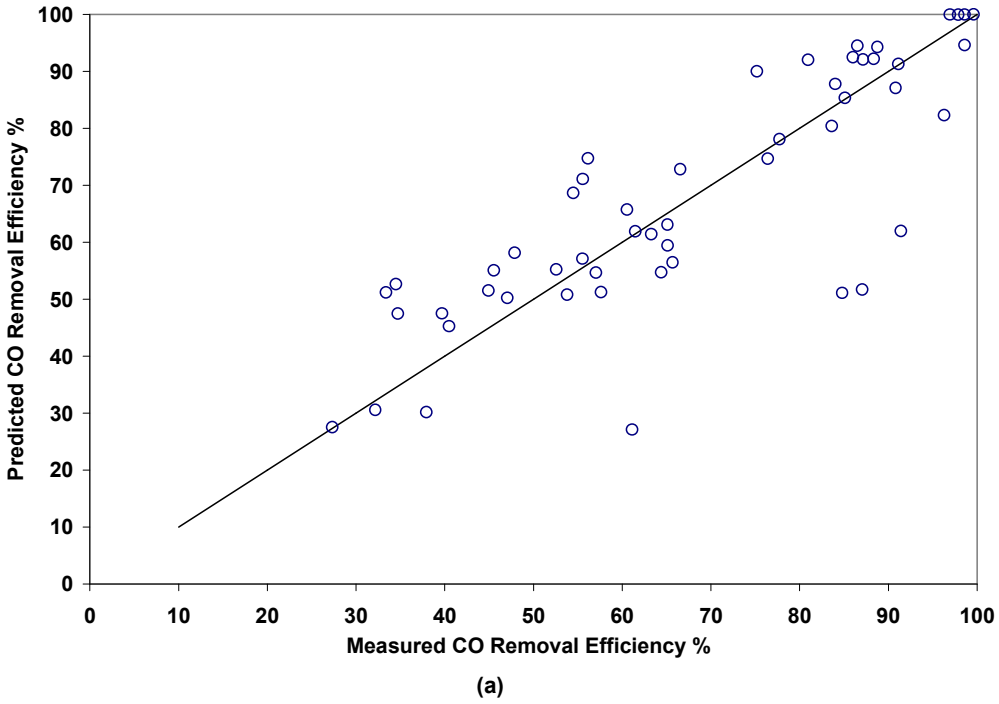


(a)

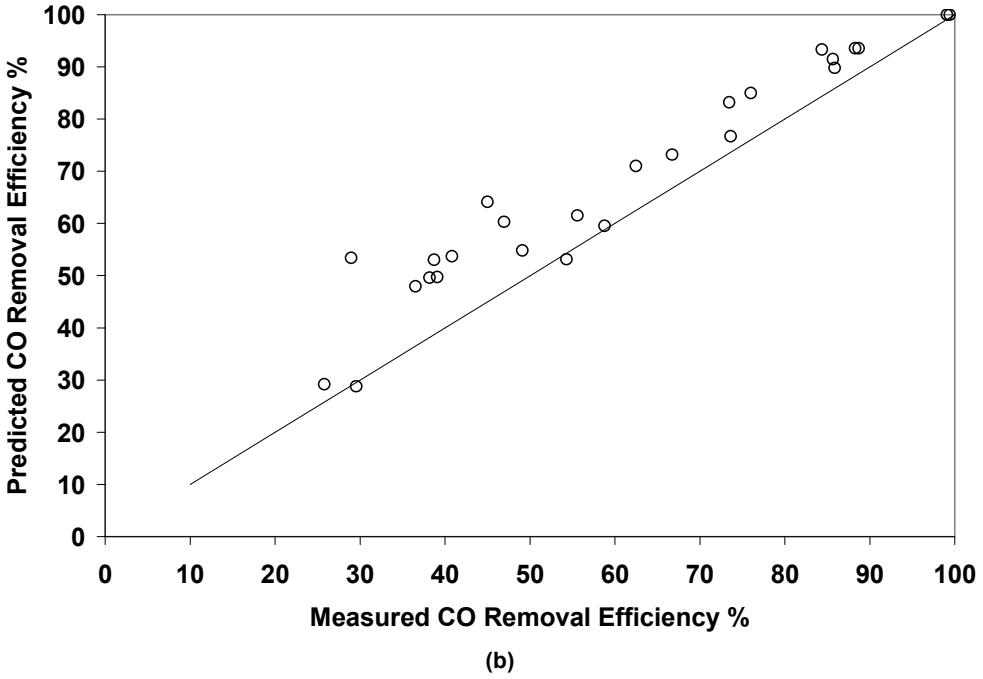


(b)

Figure 3.2: (a) Model calibration of batch/bottle CO experiment on compost #2 and #4 showing measured versus predicted removal efficiencies and (b) Validation of compost #2 and #4 models on data from compost #6.



(a)



(b)

Figure 3.3: (a) Model calibration of batch/bottle CO experiment on pebble #1 and #3 showing measured versus predicted removal efficiencies and (b) Validation of pebble #1 and #3 models on data from pebble #5.

Figure 3.4 and 3.5 are visual representations of the difference in the modeled performance of the two media under increasing exposure time and maturity time respectively. The compost model considered all observed data from compost biofilters #2, #4 and #6 for model fitting with coefficient A as 0.0901 and coefficient B as 0.2248 in Equation 2.4. The pebble model considered all data from pebble biofilters #1, #3 and #5 for model fitting with coefficients for A and B calculated as 0.0254 and 0.04732 respectively.

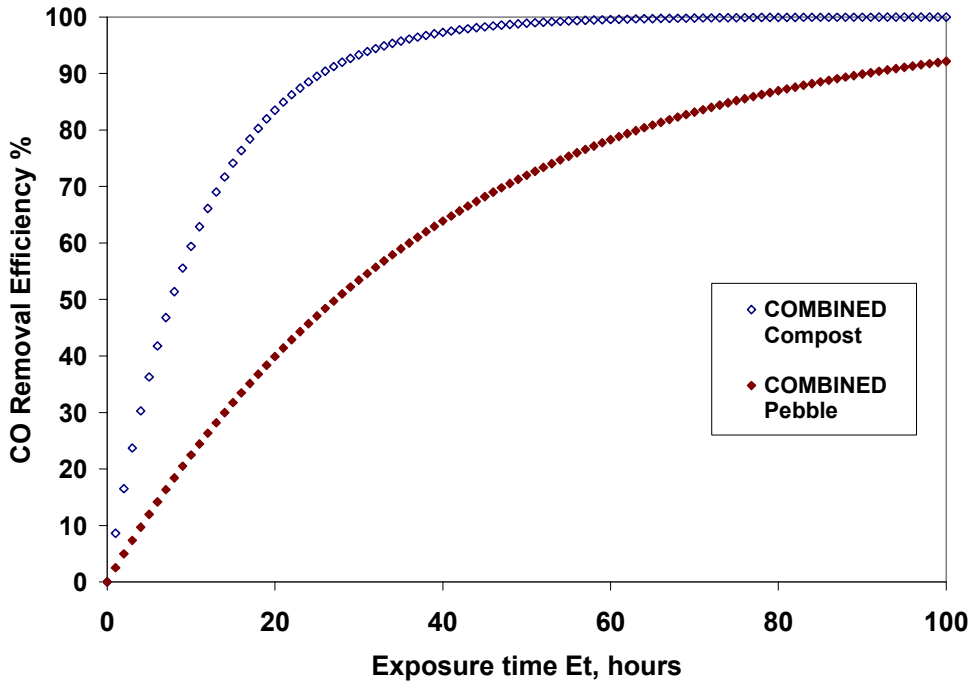


Figure 3.4: Comparison of modeled performance of the compost and pebble media as a function of increasing exposure time under a constant maturity time of 1 day. The models were based on Equation 2.4, and all data from three replicates for each media were used for model fitting.

In figure 3.4, we can see the model response to exposure time. The rate of increase in CO removal for the compost model reaches steady state after 40 hour exposure, while the pebble media did not reach steady state after 100 hours. The

combined compost model removed 98% CO in 40 hours while the pebble media only removed 60%.

The effect of increasing maturity, on CO removal efficiencies for the biofilters over 100 days of regular exposure (8 hours) was also plotted for both media in Figures 3.5. The biofilters were assumed to be operating at a constant exposure time of 8 hours every day. Figure 3.5 compares the how the models of the two media perform under increasing maturity time and at a constant exposure time of 8 hours. The CO removal on Day 1 for the compost model was 50%, which was more than double the 20% of the pebble media. The removal efficiency increased with maturity time reaching 87% for the compost model and 83% for the pebble media at 100 days.

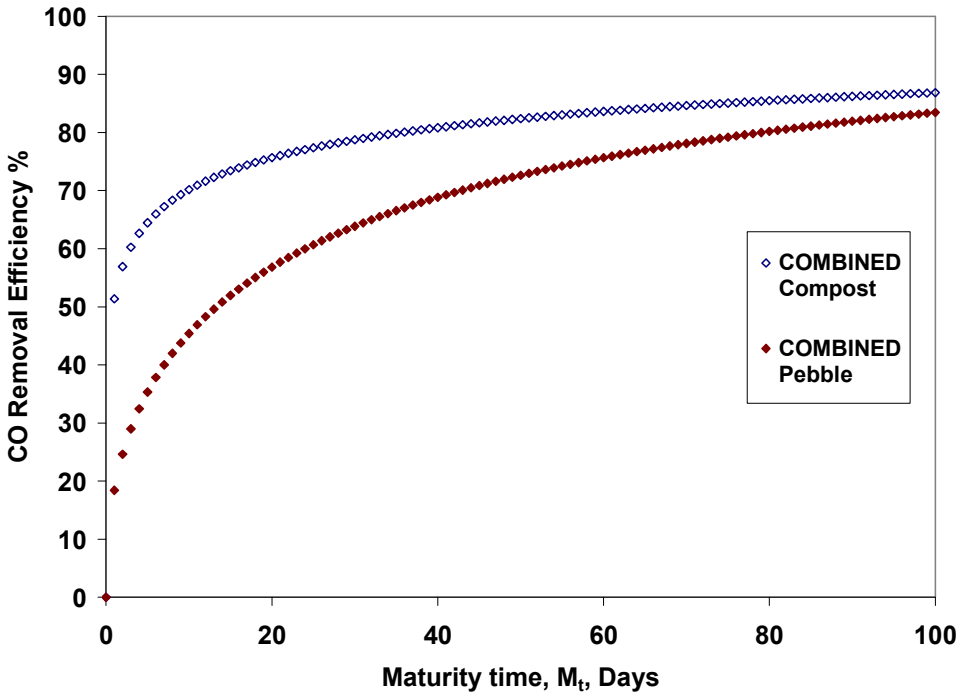


Figure 3.5: Comparison of modeled performance of the compost and pebble media as a function of increasing maturity time under a constant exposure time of 8 hours. The models were based on Equation 2.4, and all data from three replicates for each media were used for model fitting.

3.1.3 Continuous Loading of Biofilters with Bottled CO

Mean daily outlet concentration of CO of biofilter # 6, loaded with bottled CO at 1008 ppm, is shown in Figure 3.6. The inoculations on Day 5 and Day 25 are marked on the graph. Figure 3.6 visually represents how the steady state CO

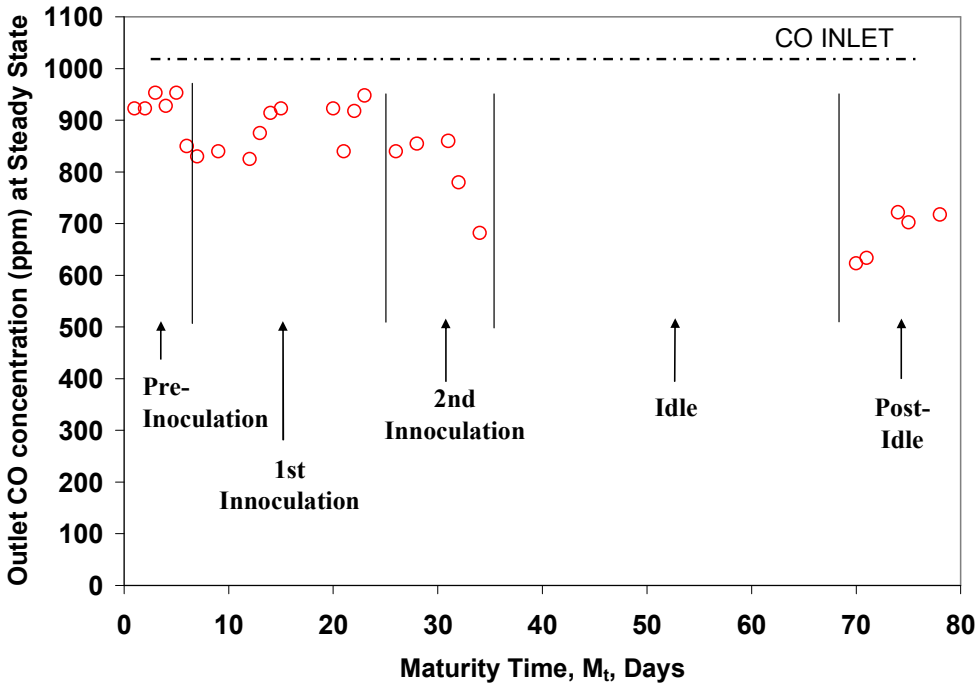


Figure 3.6: CO steady state outlet concentration from biofilter #6 through the 78 day experiment.

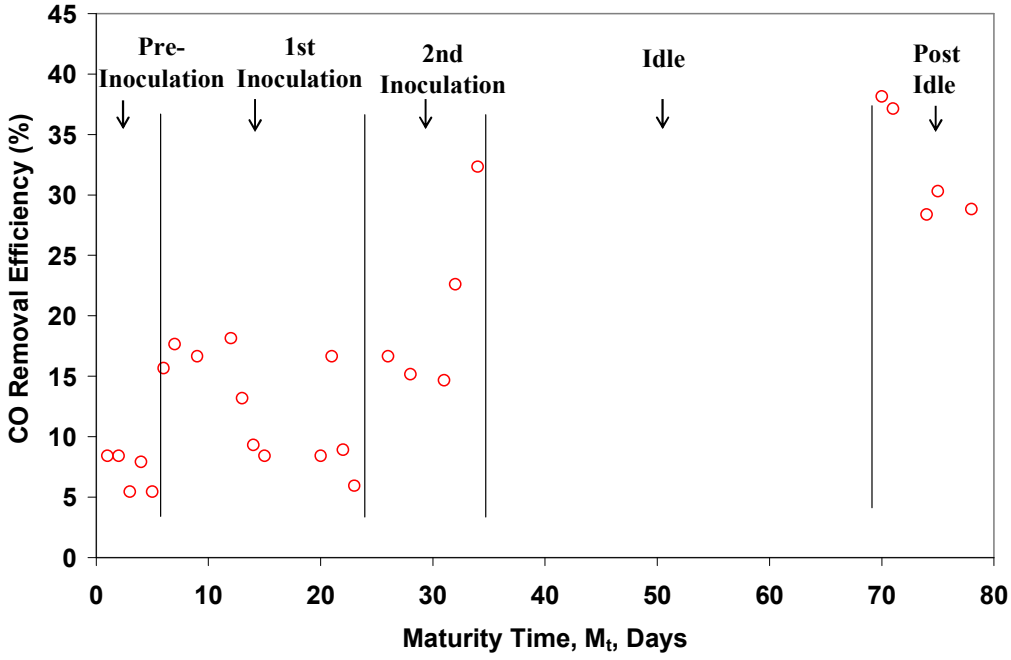


Figure 3.7: CO removal efficiency of compost biofilter # 6 after various treatments of inoculation and idleness.

concentration is immediately lowered with inoculations. The improvement in CO removal is also evident with increasing maturity of the biofilter.

The change in removal efficiencies over the 78 day run with the effect of inoculation and idle conditions on the compost biofilter is plotted in Figure 3.7. After the 1st inoculation on Day 5 the removal efficiency increased from 5% to 16%. After Day 12, the removal efficiency began to go back down before the biofilter was inoculated for a second time. Immediately after the second Inoculation, the efficiency jumped from 6% to 17% and continued to increase to 35% on Day 35. After 35 days of idleness, the removal efficiency increased slightly from 32% to 38%.

Table 3.4 summarizes the average outlet CO concentration for all the stages of the continuous/bottle experiment. The average steady state outlet concentration at the start of the experiment was 931 ppm-CO, which dropped to an average of 878 ppm after the 1st inoculation. There was further reduction to 803 ppm after the 2nd inoculation. After the idle period of 35 days, the compost biofilter showed an average outlet CO concentration of 679 ppm. The average mass of CO removal (Equations 2.6, 2.7 and 2.8) increased from 0.043 mg/hr to 0.203 mg/hr after 65 operational days.

Table 3.5 summarizes how much compost biofilter (#6) improved with each inoculation or idle period. Each inoculation improved CO removal by the biofilter more than the previous one.

Figure 3.8 graphs the increase in CO mass removal as the biofilter was treated with innoculum. The mass of CO removed remained high after the idle period of 35 days.

Table 3.4: CO steady state dynamics through 78 day run

Period	Inlet CO ppm	Average Steady State CO ppm at outlet	Decrease in CO (ppm)	Average rate of CO removal (mg/hr)
Pre-Inoculation	1008	931	77	0.043
1st Inoculation	1008	878	130	0.075
2nd Inoculation	1008	803	205	0.127
Idle Post-Idle	1008	679	329	0.203

Table 3.5: Improvement in CO removal

Period Comparison	Reduction in Average Steady State CO ppm
Pre-inoculation – 1st inoculation	52.83
1st inoculation – 2nd inoculation	75.52
2nd inoculation – Post idle	123.61

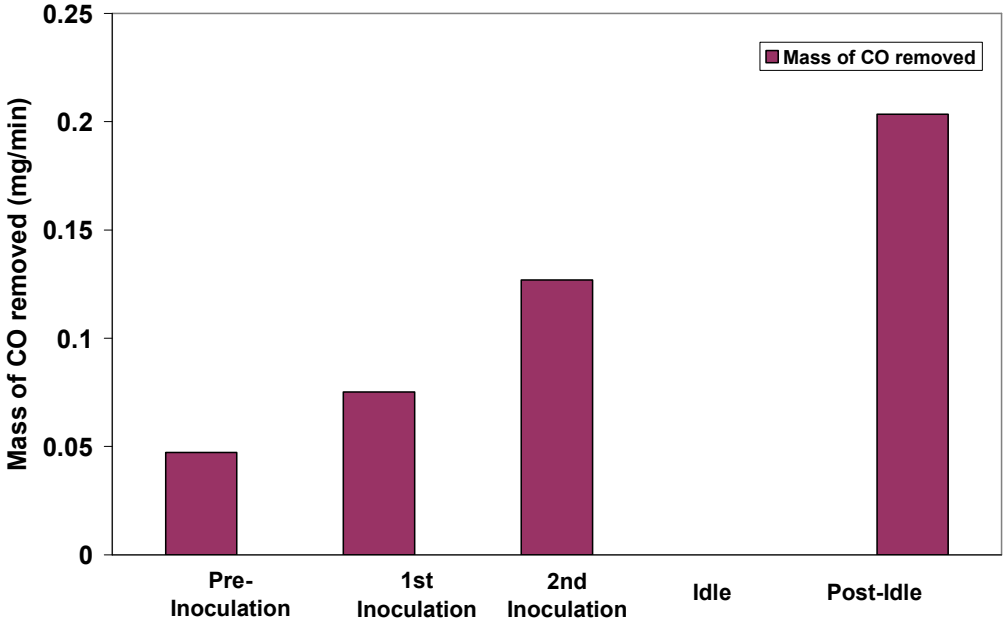


Figure 3.8: CO mass removal after each inoculation and idle period.

3.1.3 Exhaust CO Removal by Biofilters under Continuous Loading

This section reports the inlet and outlet concentrations for the compost and pebble biofilters, treating engine exhausts at 1000 ppm–CO (CM2, PM3) and at 700 ppm-CO (CM4 and PM1) before and after soil inoculations. The variable inlet CO from engine exhausts, read at intervals of approximately 30 minutes, were averaged

and plotted together with outlet CO concentrations as time series to visualize removal.

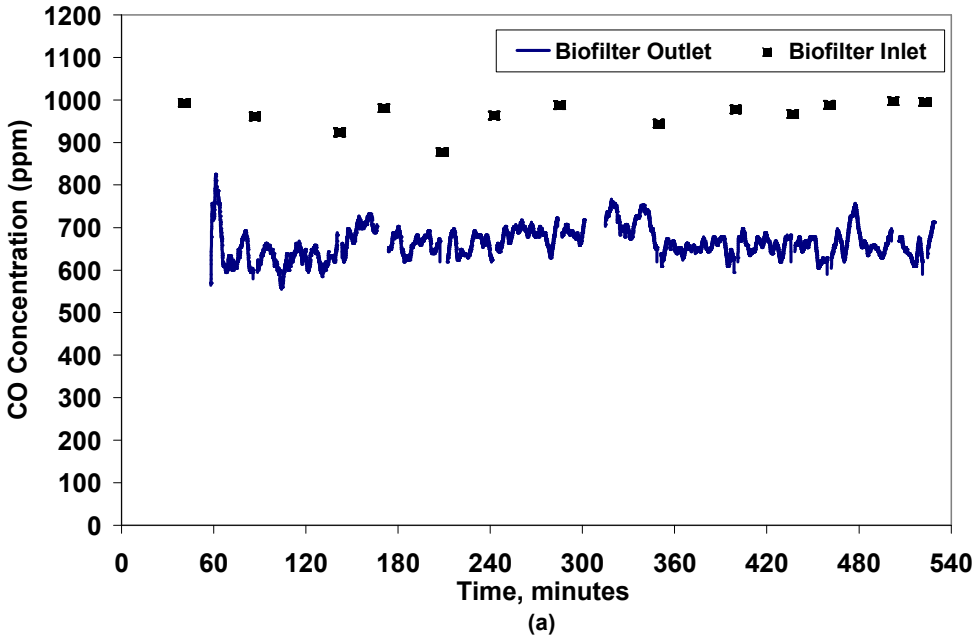
Figure 3.9 compares CM2 and PM3 biofilters receiving CO targeted at 1000 ppm from engine exhausts during their first test before any inoculation with soil slurries. The CM2 biofilter showed higher mean removal efficiency of 31.23 % (Table 3.5) than the PM3 biofilter which removed a mean of 19.6 % (Table 3.5) CO.

The second run on CM2 biofilter and PM3 biofilter without soil inoculation is plotted in Figure 3.10. The CM2 biofilter continued to perform better than the pebble biofilter (PM3) demonstrating 11.0% mean CO removal as compared to 8.1% of the pebble biofilter (PM3). Both media showed lower removal efficiencies than test 1 (Table 3.5).

Figure 3.11 is a plot of inlet and outlet concentrations from CM2 and PM3 biofilters after they were inoculated with soil slurries for a third test receiving engine exhaust at 1000 ppm of CO. There was an immediate improvement in removal efficiency for CM2 biofilter after inoculation which showed 44.9% removal. The pebble biofilter PM3 also performed better than the previous run, removing 11.1 % CO (Table 3.5).

CM2 biofilter and the pebble PM3 biofilter were continued to be tested with engine exhausts. Figure 3.12 graphs the inlet and outlet CO concentrations of the 4^{th} test. No additional inoculations were done at this stage. The removal efficiency in the compost biofilter decreased to 28.2%, while the pebble biofilter maintained a removal efficiency of 11.2% (Table 3.5).

Figure 3.13a and b, help to visualize the performance of the compost CM2 and PM3 biofilters fed engine exhaust over the course of the experiment. The compost biofilter CM2 shows higher removal than the pebble biofilter.



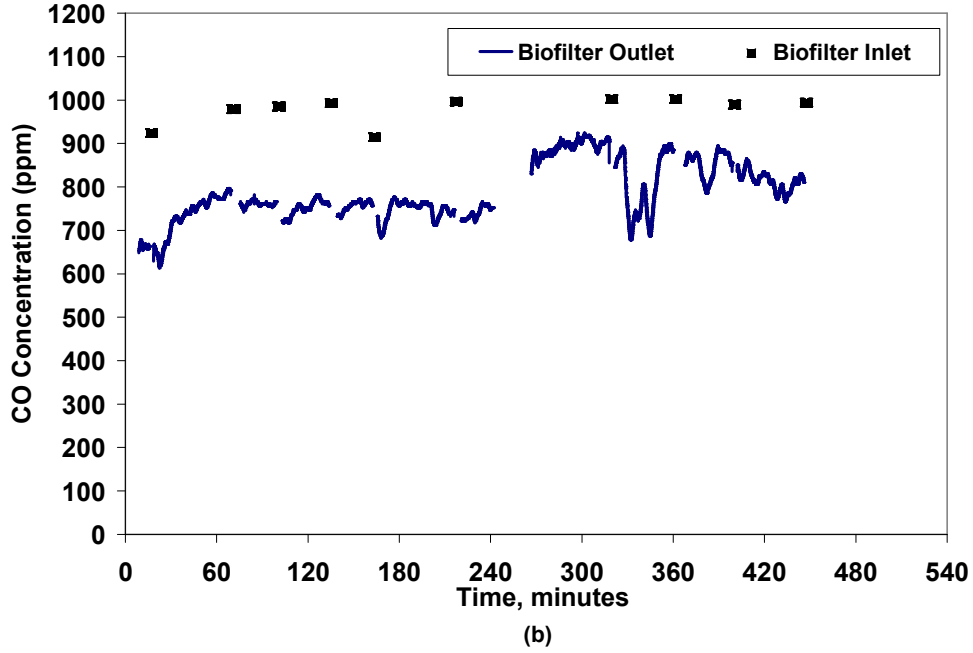
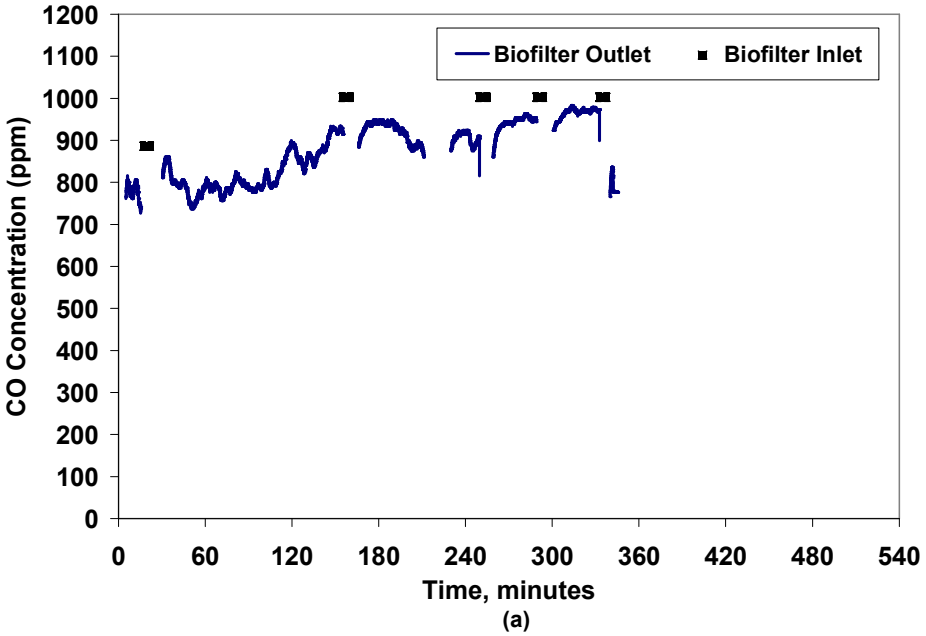


Figure 3.9: Inlet and outlet CO concentration for the a) compost biofilter CM2 (on 7/10/2003) and b) pebble biofilter PM3 (on 7/11/2003) receiving engine exhausts targeted at 1000 ppm-CO, before inoculation.



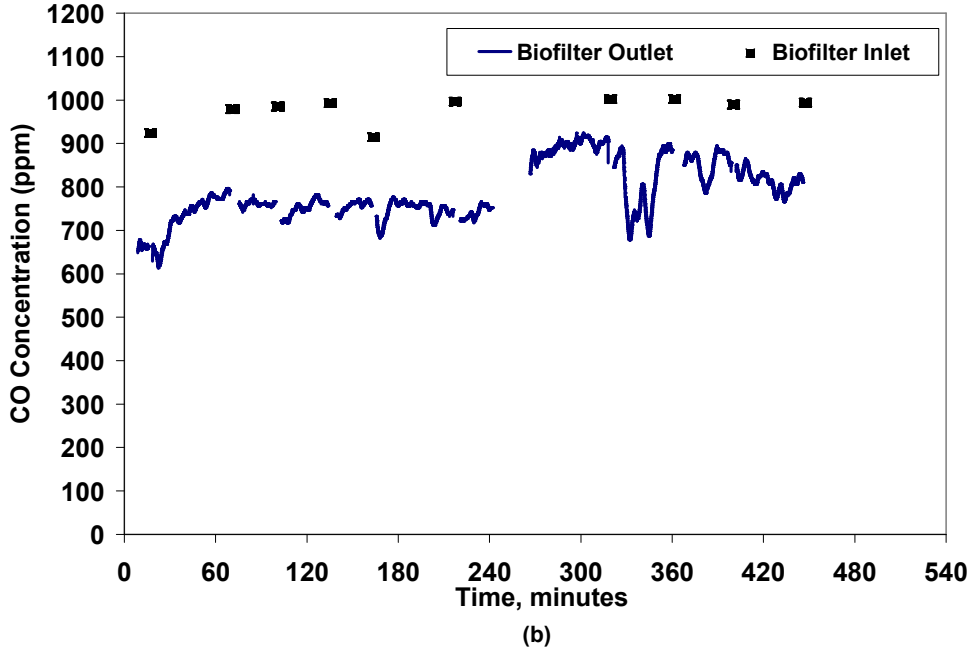
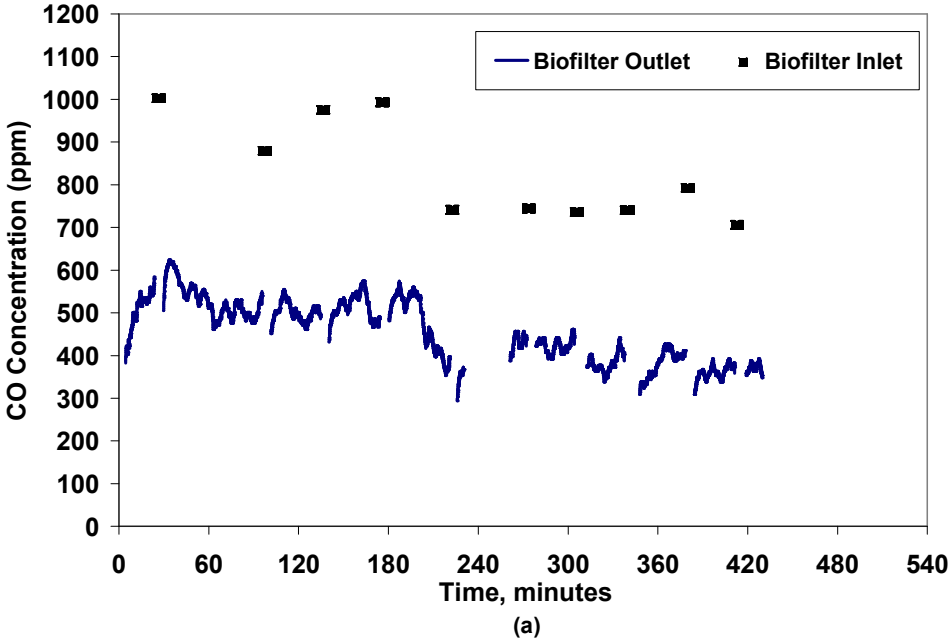


Figure 3.10: Inlet and outlet CO concentration for the a) compost biofilter CM2 (on 7/29/2003) and b) pebble biofilter PM3 (on 7/28/2003) receiving engine exhausts targeted at 1000 ppm-CO, before inoculation.



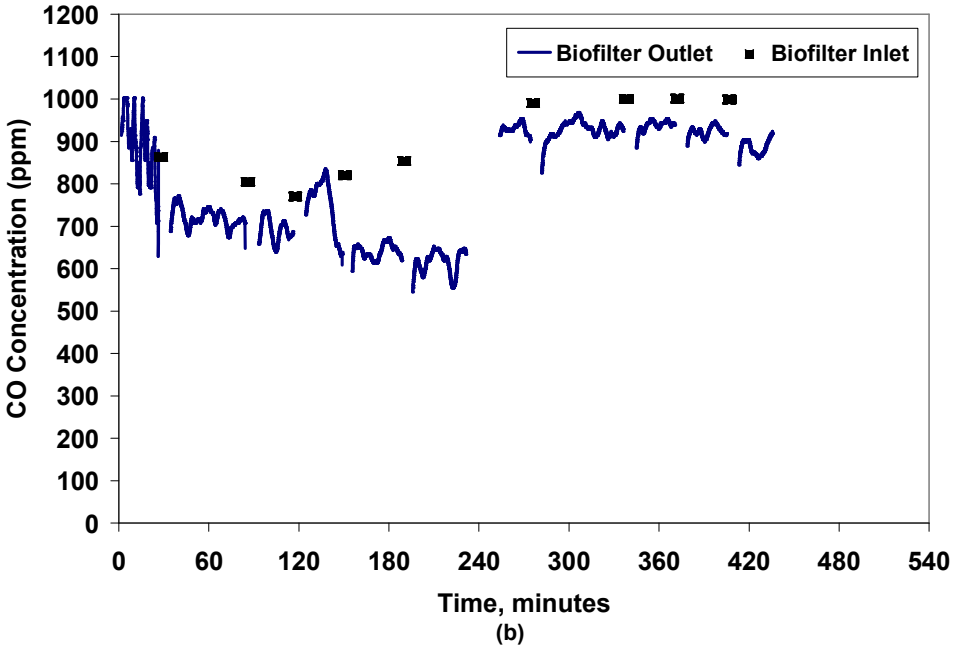
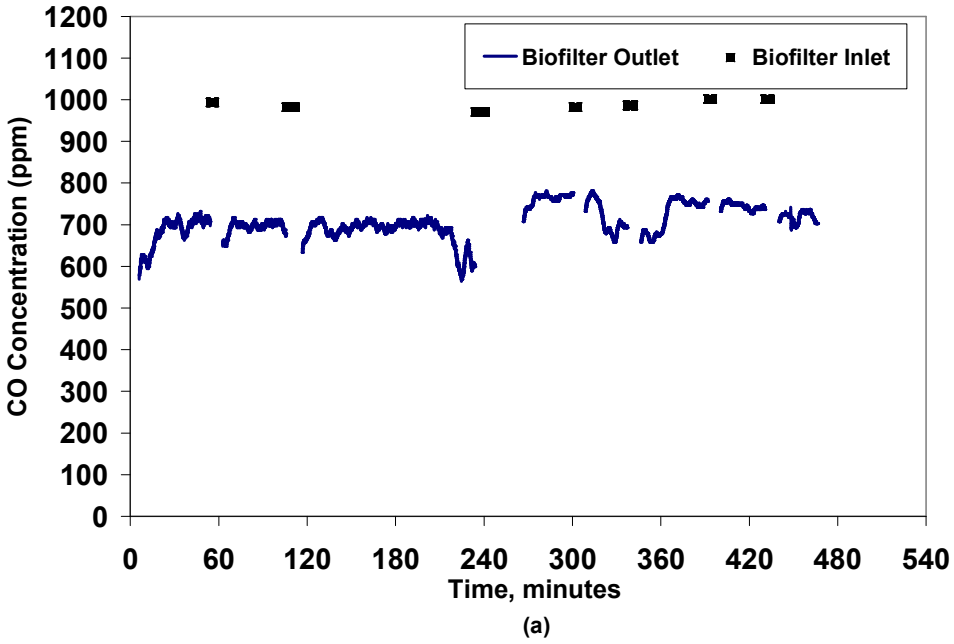


Figure 3.11: Inlet and outlet CO concentration for the a) compost biofilter CM2 (on 8/1/03) and b) pebble biofilter PM3 (on 8/4/03) receiving engine exhausts targeted 1000 ppm-CO, after inoculation.



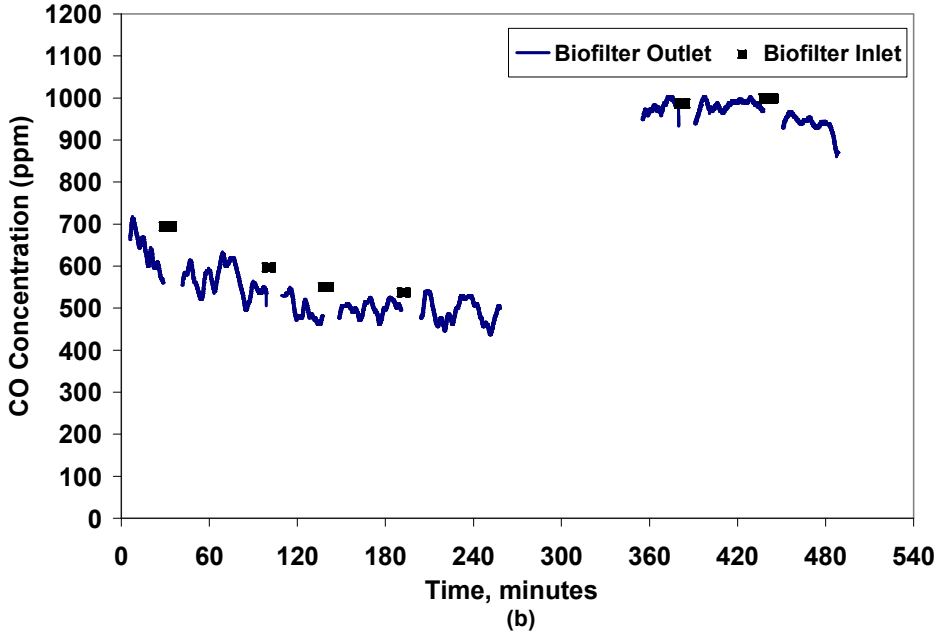


Figure 3.12: Inlet and outlet CO concentration for the a) compost biofilter CM2 (on 8/14/03) and b) pebble biofilter PM3 (8/13/03) receiving engine exhausts targeted at 1000 ppm-CO, after inoculation.

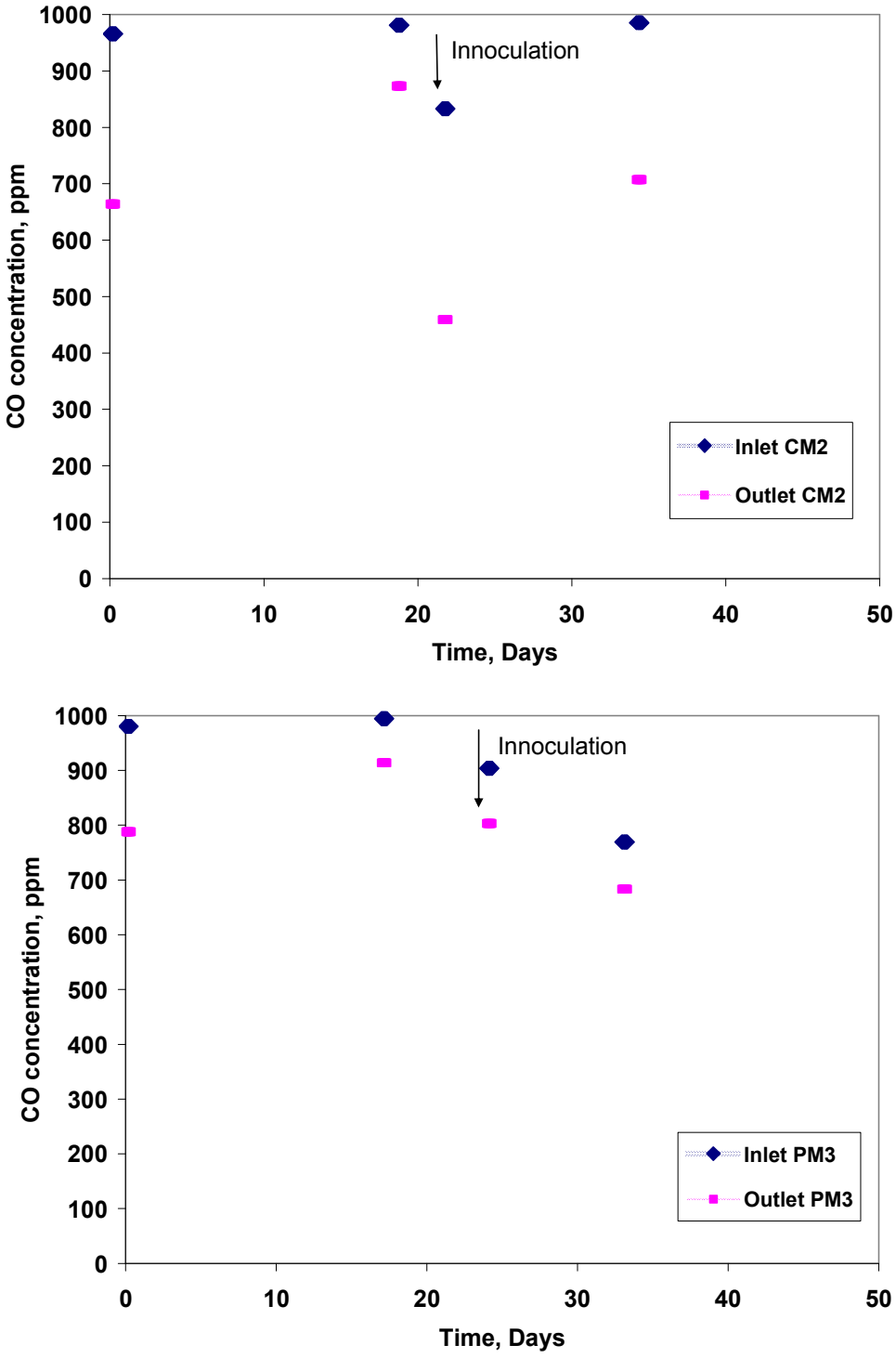


Figure 3.13: Mean daily input and output CO concentration of (a) Compost CM2 and (b) Pebble PM3 before and after inoculation when continuously fed engine exhaust @1000 ppm CO.

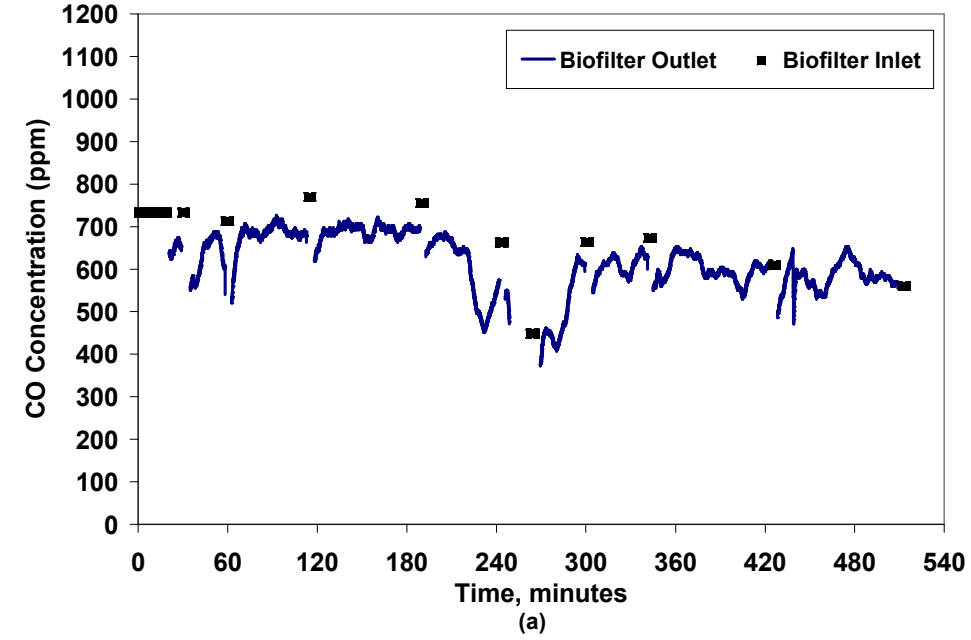
Figure 3.14 shows the inlet and outlet concentrations for the CM4 biofilter and PM1 biofilter treating engine exhausts at 700 ppm-CO. During this first test, the CM4 did better than the pebble biofilter removing a mean of 10.1% CO.

The second test for the compost and pebble biofilters (Figure 3.15) also shows the CM4 compost biofilter doing better than the pebble biofilter PM1 in terms of CO removal efficiency. The compost biofilter removed a mean of 13.1% CO, while the pebble biofilter removed a mean of 3.2% CO.

Figure 3.16 shows the third test of engine exhausts through the CM4 and pebble PM1 biofilters. The biofilters were inoculated with soil slurries before the start of this run. Both the biofilters demonstrated very low mean CO removal efficiencies of 0.42% and 0% respectively (Table 3.5).

The input and output CO concentrations of the CM4 and PM1 biofilters are plotted in Figure 3.17. This was the 4^{th} test for both biofilters receiving engine exhausts with 700 ppm CO. The compost biofilter showed a mean removal efficiency of 16.9%, compared to a 2.8% mean removal demonstrated by the pebble biofilter (Table 3.5).

Figure 3.18 show how the compost and pebble biofilters (CM4 and PM1 respectively) remove CO from engine exhaust at 700 ppm-CO. The average inlet and outlet CO concentrations were plotted for each media under each test. The compost biofilter performed better than the pebble biofilter, under the same conditions.



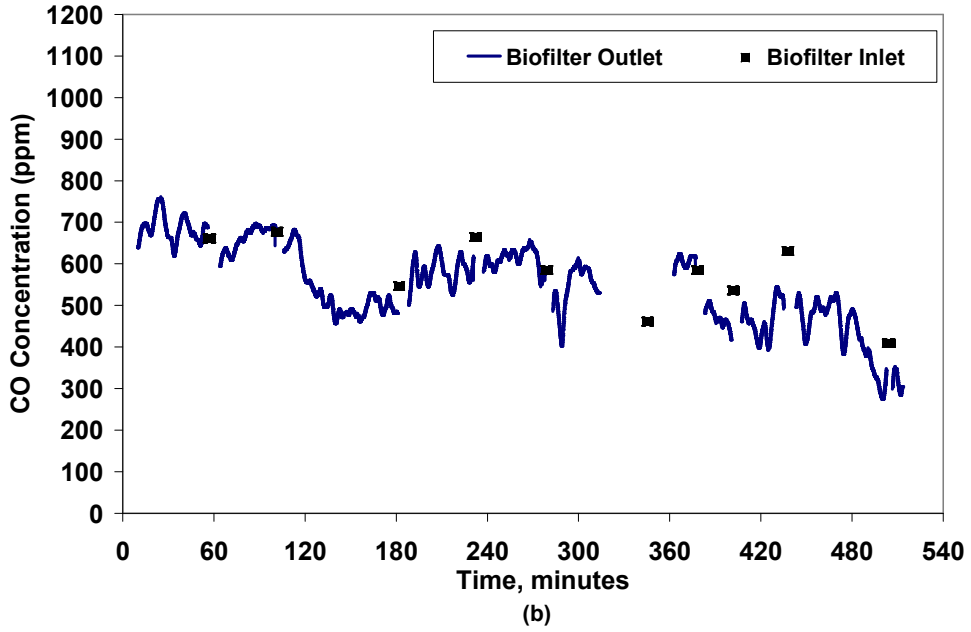
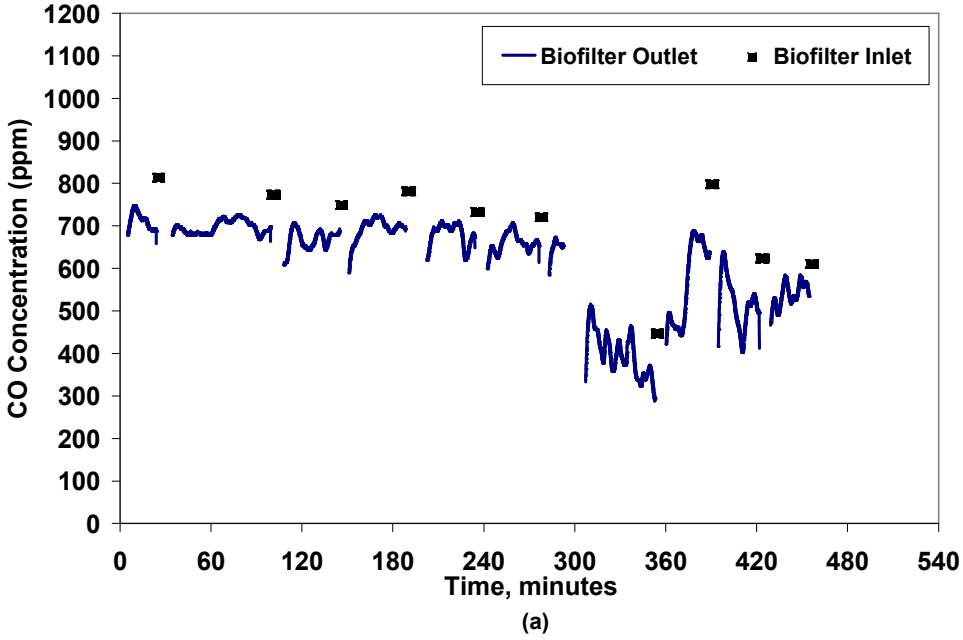


Figure 3.14: Inlet and outlet CO concentration for the a) compost biofilter CM4 (on 7/14/03) and b) pebble biofilter PM1 (on 7/9/03) receiving engine exhausts targeted at 700 ppm-CO, before inoculation.



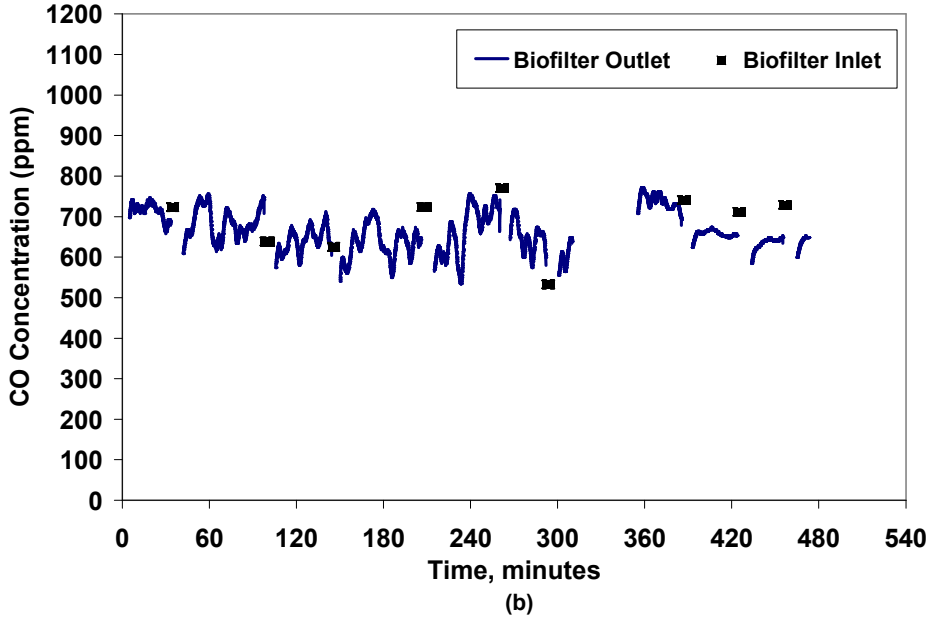
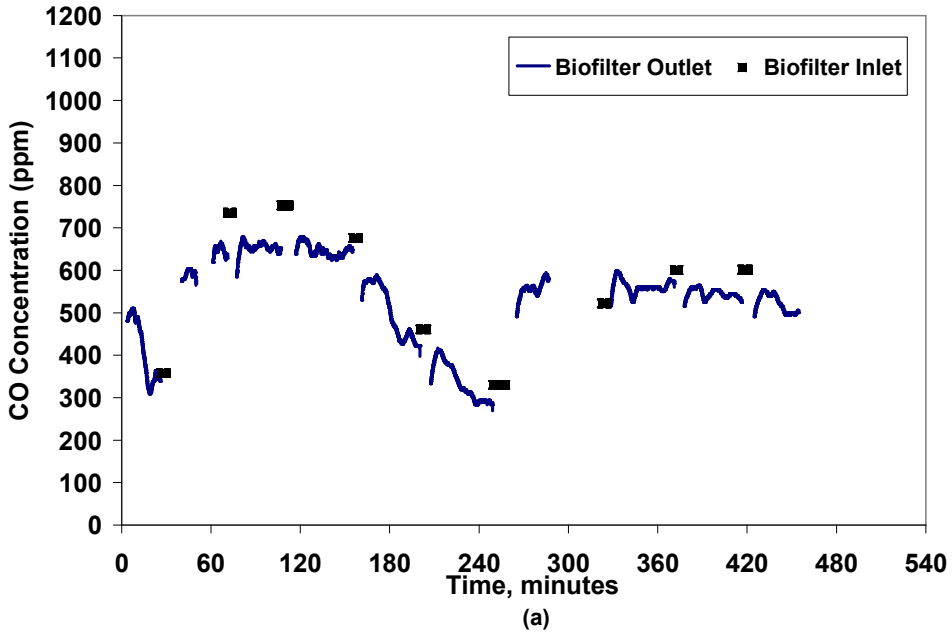


Figure 3.15: Inlet and outlet CO concentration for the a) compost biofilter CM4 (on 7/24/03) and b) pebble biofilter PM1 (on 7/23/04) receiving engine exhausts targeted at 700 ppm-CO, before inoculation.



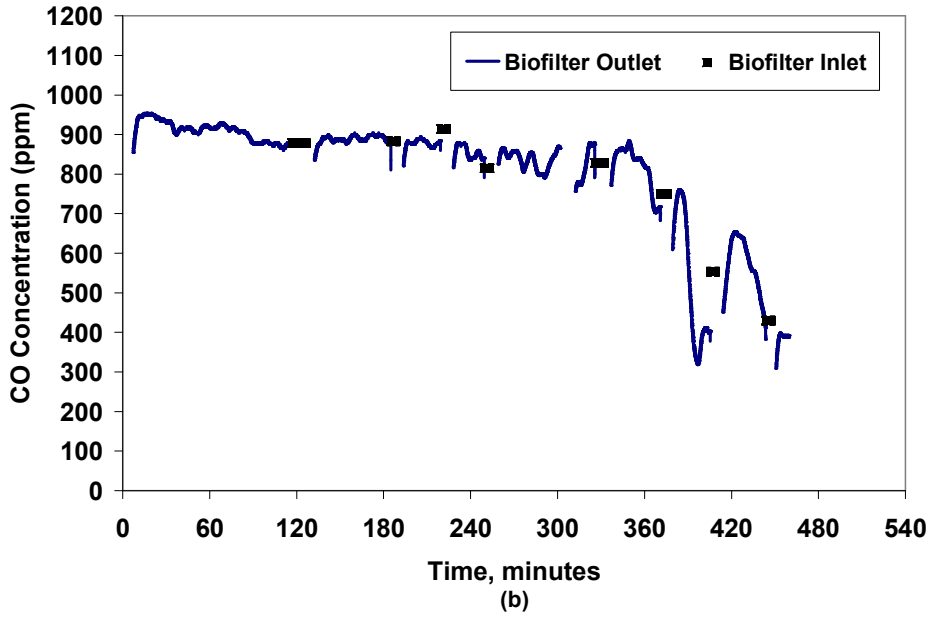
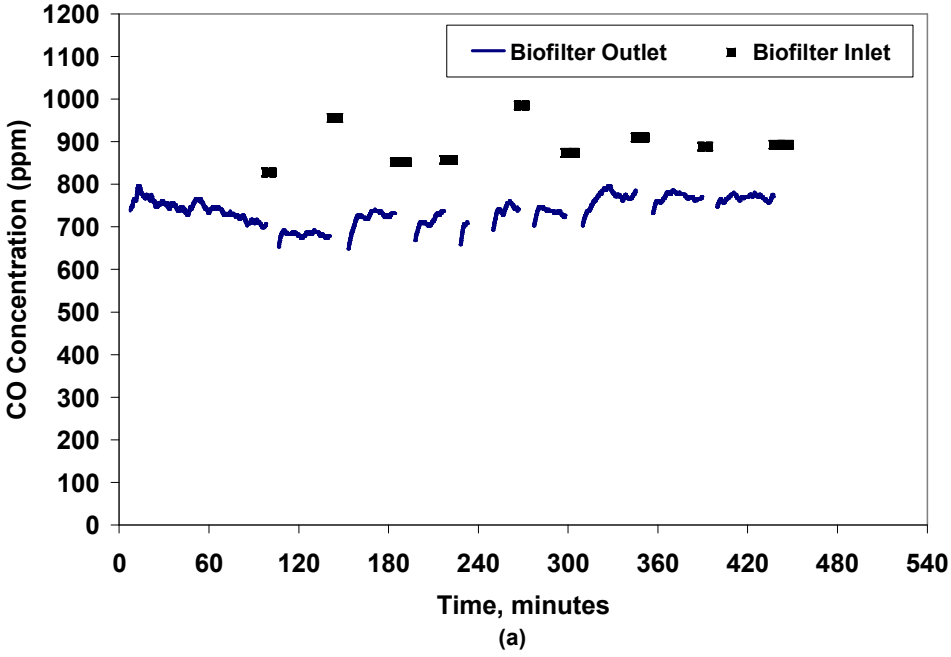


Figure 3.16: Inlet and outlet CO concentration for the a) compost biofilter CM4 (on 8/6/03) and b) pebble biofilter PM1 (on 8/7/03) receiving engine exhausts targeted at 700 ppm-CO, after inoculation.



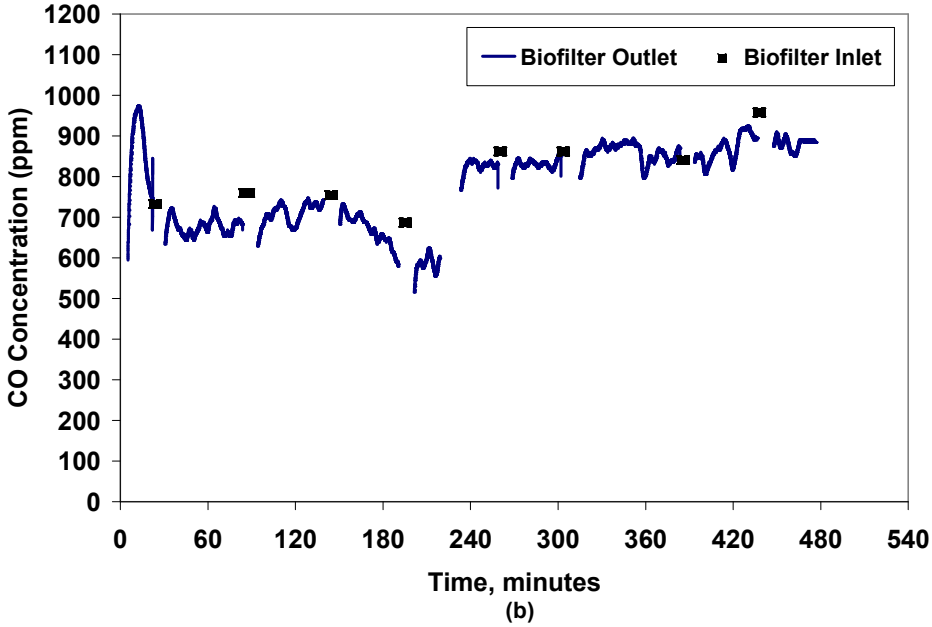
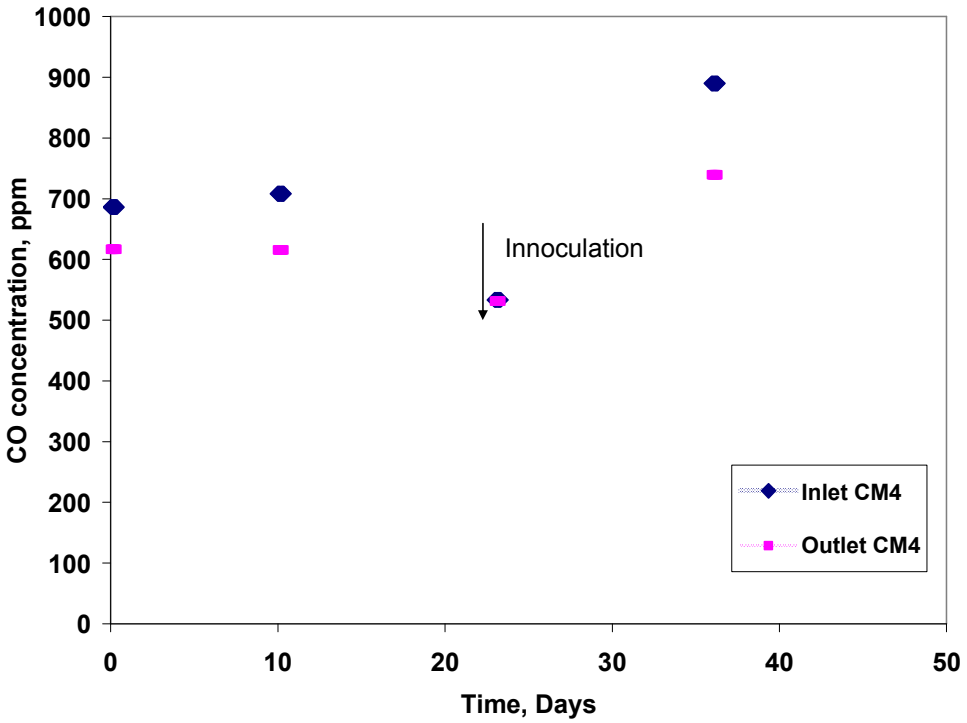


Figure 3.17: Inlet and outlet CO concentration for the a) compost biofilter CM4 (on 8/19/03) and b) pebble biofilter PM1 (on 8/18/03) receiving engine exhausts targeted at 700 ppm-CO, after inoculation.



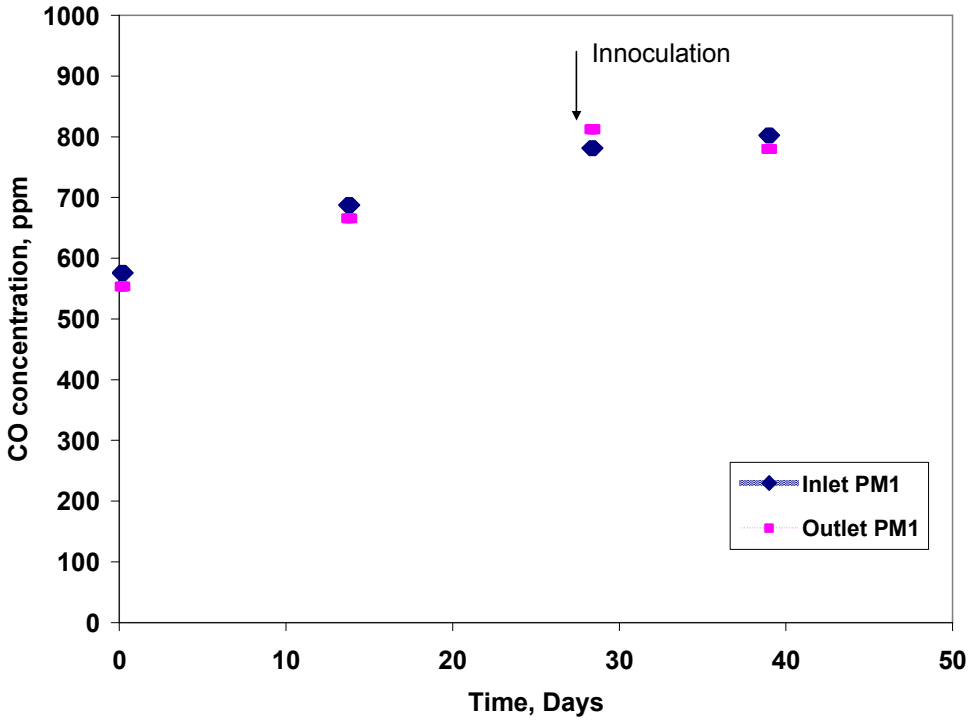


Figure 3.18: Mean daily input and output CO concentration of (a) Compost CM4 and (b) Pebble PM1 before and after inoculation when continuously fed engine exhaust @700 ppm CO.

The removal efficiencies for each biofilter were calculated for every test according to Equation 2.1 and summarized (Table 3.6).

Table 3.6: Mean daily CO removal efficiencies (%) for compost and pebble media, loaded with engine exhausts

	Inlet exhaust at 1000 ppm-CO		Inlet exhaust at 700 ppm –CO	
Run	**Compost CM2**	**Pebble PM3**	**Compost CM4**	**Pebble PM1**
1 (No Inoc)	31.2	19.6	10.1	3.9
2 (No Inoc)	11.0	8.1	13.1	3.2
3 (Inoc)	44.9	11.1	0.4	0.0
4 (Inoc)	28.2	11.2	16.9	2.8

The CO mass uptake (mg/hr) for each run and each biofilter, calculated from Equations 2.4, 2.5 and 2.6, was plotted as a bar chart (Figure 3.19 and Figure 3.20) comparing the compost and pebble media performance at the 700 ppm level and 1000 CO-ppm level.

Figure 3.19 shows the mass uptake (mg/hr) for the compost #2 and the pebble #3 biofilter receiving engine exhausts at 1000 ppm CO. Tests 1 and 2 were before inoculations and tests 3 and 4 were after inoculation. The compost biofilter showed higher levels of CO mass uptake for all tests at the 1000 ppm CO level. The compost biofilter CM2 showed a large increase in CO uptake in test 3, as compared to test 2 (Figure 3.19). The pebble biofilter PM3 started at 0.29 mg/hr of CO removal, but then decreased to 0.12 mg/hr and remained nearly level for the remaining tests. Figure 3.20 compares the CO uptake of the compost CM4 and the pebble PM1 biofilters at 700 ppm. The compost biofilter showed a higher CO uptake for all the tests. The pebble biofilter removed approximately the same mass of CO for all the tests despite inoculation after test 2. The compost biofilter CM4 showed steadily increasing mass uptake for all runs except test 3 which showed no uptake for both compost and pebble biofilters.

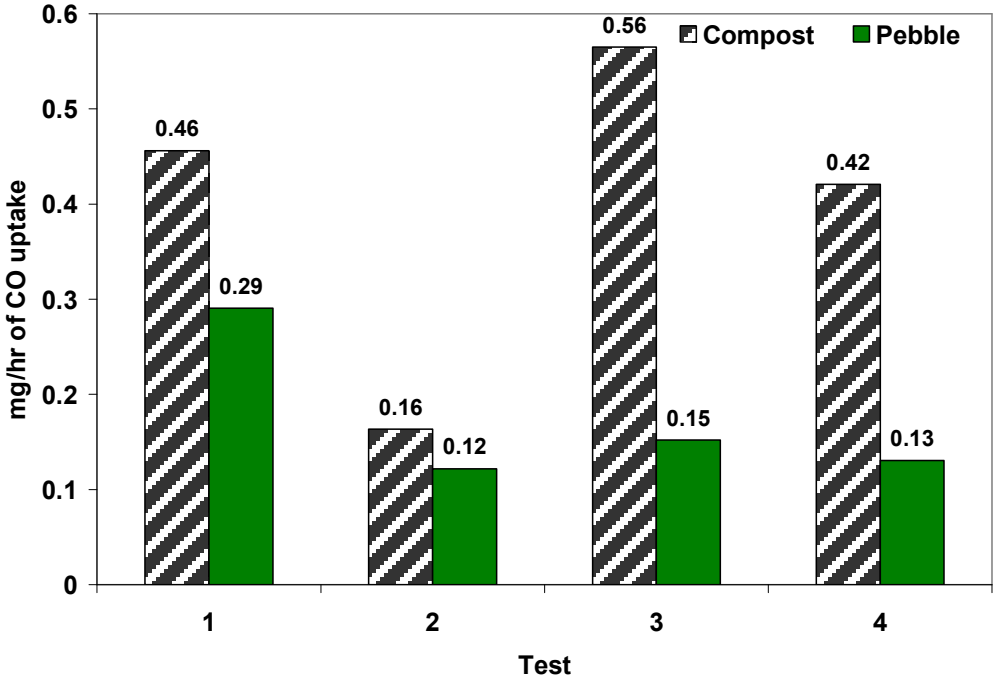


Figure 3.19: CO mass uptake by the compost CM2 and pebble PM3 filters for each run, from engine exhaust targeted at 1000 ppm-CO.

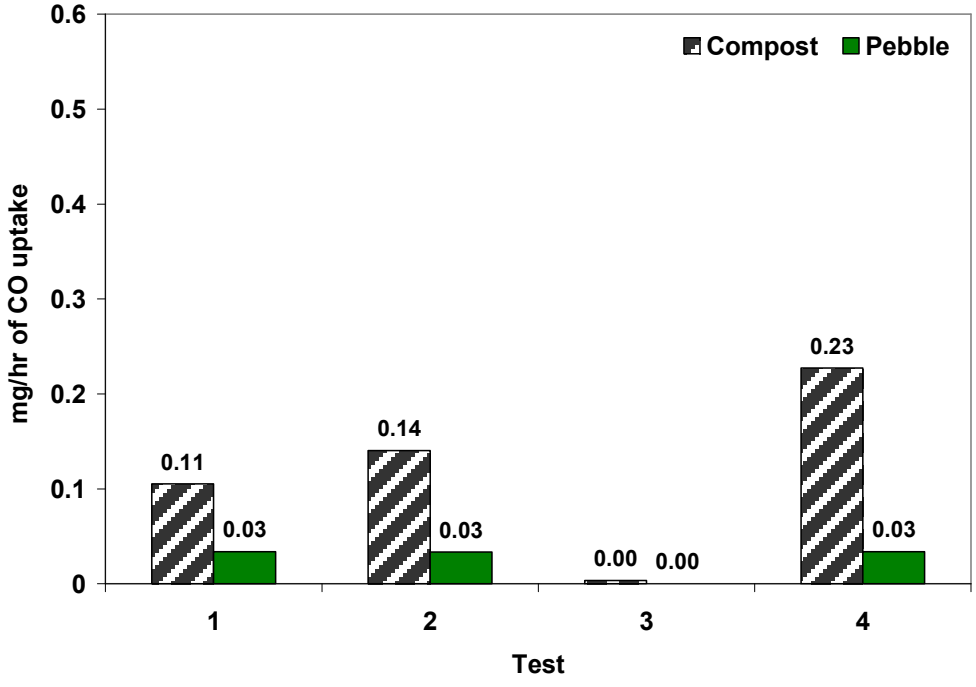


Figure 3.20: CO mass uptake by the compost (#4) and pebble (#1) filters for each run, from engine exhaust targeted at 700 ppm-CO.

Table 3.7 summarizes the three-way anova test carried out on the mass removed by the compost and pebble media for the two pollutant concentration levels (700 ppm and 1000 ppm) under inoculated or not inoculated conditions. We can see that the two-way interactions between pollutant concentration, media and inoculation are not significant at the 5% level. Also the three-way interaction between pollutant concentration, media and inoculation is not significant (Table 3.7).

Table 3.7: Three-way ANOVA on the CO mass removed by compost and pebble biofilters loaded with CO exhaust at 700 and 1000 ppm-CO

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.346	7	.049	4.182	.031
Intercept	.516	1	.516	43.713	.000
PollConc[X]	.187	1	.187	15.803	.004
Media[X]	.103	1	.103	8.698	.018
Innoc	.002	1	.002	.179	.683
PollConc * Media	.018	1	.018	1.543	.249
PollConc * Innoc	.005	1	.005	.433	.529
Media * Innoc	.016	1	.016	1.387	.273
PollConc * Media * Innoc	.015	1	.015	1.230	.300
Error	.094	8	.012		
Total	.956	16			
Corrected Total	.440	15			

[X]- significantly different at α=0.05

Table 3.8 displays the mean CO mass removal for the biofilters treating CO engine exhaust. The CO pollutant concentration, i.e. the CO loading of 1000 ppm or 700 ppm is shown to be a significant factor in the difference in CO mass removal ($p<0.05$) (Table 3.7 and 3.8). The biofilter media, whether compost or pebble was also determined to be a significant factor at the 5% level. Inoculation turned out not significant in the mass removal for the biofilters.

Table 3.8: Mean CO mass removal (mg h^{-1}) by compost and pebble biofilters loaded with CO exhaust at 700 and 1000 ppm-CO under different factors.

	Mean Mass Removal ±Standard Error
Pollutant Concentration	
700	0.072 ±0.038
1000	0.288 ±0.038
Significance at 5%	0.040
Media	
Compost	0.260±0.038
Pebble	0.100±0.038
Significance at 5%	0.018
Inoculation	
Yes	0.191±0.038
No	0.168±0.038
Significance at 5%	0.683

3.1.4 Effect of Chlorination

Figure 3.21 shows the results of the chlorination experiment on compost biofilter #6. The steady state CO concentration levels are plotted before and after chlorination. The steady state outlet CO concentration decreased during the pre-chlorination period, demonstrated by the regression line (Figure 3.21). After chlorination the biofilter outlet CO increased to 97 ppm- CO within 2 days.

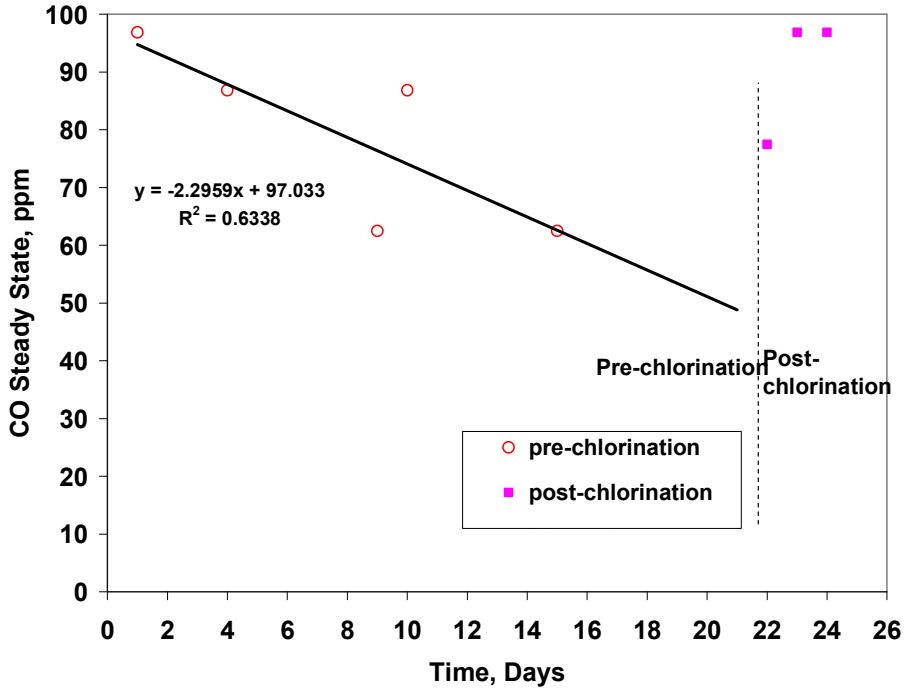


Figure 3.21: Outlet CO concentration from compost biofilter # 6, continuously loaded with bottled CO at 100 ppm, before and after chlorination.

3.2 Emergy Analysis

The emergy evaluation of the lab-scale biofilter, pilot-scale biofilter and catalytic converter are reported in this section. Compost (media), electricity, construction materials and labor were the main emergy inputs required to make and operate the biofilter setup (Figure 3.22). Emergy inputs of the catalytic converter included rare metals, fuel consumption, electricity use, materials and labor (Figure 3.23).

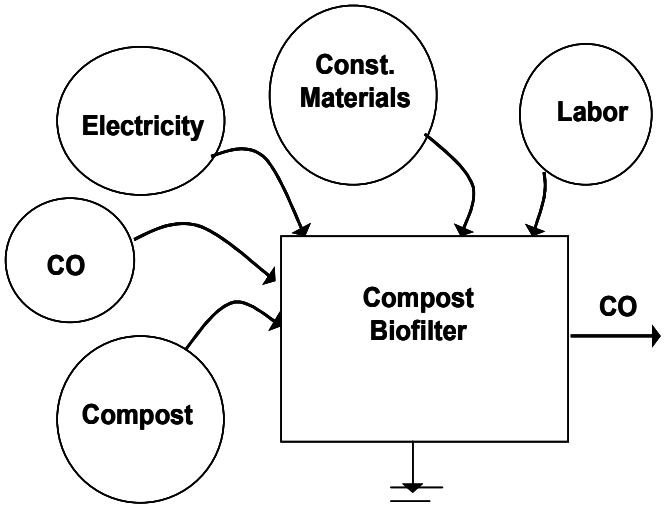


Figure 3.22: Emergy systems diagram for a compost biofilter setup.

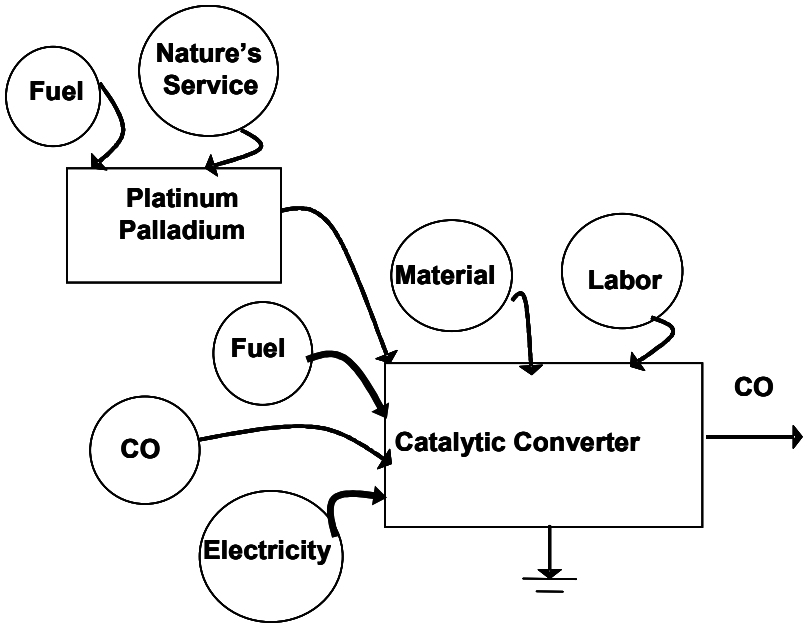


Figure 3.23: Energy systems diagram for the catalytic converter.

3.2.1 Emergy Evaluation of Lab-scale System

A typical compost biofilter run (Figure 3.9), treating CO exhaust was considered to calculate CO uptake. Using data from Figure 3.9, we can calculate the

average inlet CO concentration to the biofilter (I) = 831 ppm (averaged from Figure 3.9), average outlet CO concentration from the biofilter (O) = 455 ppm (averaged from Figure 3.9). Using the average inlet and outlet CO concentration (ppm), CO mass inflow and outflow was calculated from Equations 2.6 and 2.7. Then the CO mass uptake rate of the lab-scale biofilter was calculated to be 0.53 mg/min (Equation 2.8). The mass uptake for a lifetime use of 10 years was calculated to be 661 g.

Table 3.9 shows the emergy evaluation of the compost lab-scale biofilter. Electricity used in running the vacuum pump contributed 528 E12 sej (Table 3.9). Construction material and labor costs were the next highest contributors to biofilter emergy. The total emergy of the system was calculated to be 1374E12 sej. This total emergy was used to remove 661 g of CO over a 10 year lifetime. Therefore emergy / g of CO-removed for the lab-scale biofiltration setup was computed as 2.08 E12 sej/g.

Table 3.9: Emergy evaluation of lab-scale compost biofilter treating carbon monoxide (10 year lifetime).

Note*	Item	Unit	Value	Transformation Ratios ETR /MTR/DTR	Emergy sej (E12)
1	Compost / Soil	g	6.50E+08	7.40E+04	48
2	PVC	g	4.80E+03	5.90E+09	28
3	Electricity (Vacuum Pump)	J	1.40E+10	1.70E+05	528
4	Wood	g	6.33E+03	1.21E+09	8
5	Steel	g	3.33E+03	4.20E+09	14
Capital costs					
6	Labor cost	$	3.90E+02	7.80E+11	304
7	Construction Material	$	6.10E+02	7.80E+11	476
8	Total Emergy	sej			1374
9	CO Removed	g	6.61E+02		
10	Emergy per mass of CO removed			2.08E+12	

*- calculation for each note explained in Appendix C

3.2.2 Emergy Evaluation of Pilot-Scale Biofiltration System

Table 3.10 shows the emergy evaluation of the pilot-scale biofilter. Compost and electricity used contributed 4.16E17 sej and 3.8E17 sej, respectively to the total emergy. The largest emergy input was capital investment to setup the biofiltration system, which contributed 4.29E17 sej. Maintenance and treatment costs amounted to 2.29E17 sej, which was the lowest emergy input into the system. The total emergy required by the pilot scale biofiltration unit was 14.53E17 sej. The volume specific CO removal rate of the pilot biofilter (i.e., mass of CO removed per volume of media) was assumed to be the same as the lab-scale model. Using this treatment rate, an EBCT of 70 seconds and gas flow rate of 17,000 m^3/hr, CO uptake through 10 years of operation was 1.72E+7 g (Table 3.10). Therefore, the pilot model used 8.475E+10 sej per gram of CO removed.

Table 3.10: Emergy evaluation of pilot scale compost biofilter treating CO (10 year lifetime).

Note*	Item	Unit	Lifetime Usage	Transformity Emergy / unit	Emergy sej (E17)
Non-Renewables					
11	Compost / Soil	J	5.62E+12	7.40E+04	4.16
12	Electricity Centrifugal blower	J	2.23E+12	1.70E+05	3.80
Capital costs					
13	Investment	$	550000	7.80E+11	4.29
14	Maintenance + Treatment costs	$	293488	7.80E+11	2.29
15	Total Emergy	sej			14.53
16	CO removed	g	1.72E+07		
17	Emergy per mass CO removed	sej/g		8.47E+10	

*- calculation for each note explained in Appendix C

3.2.3 Emergy Evaluation of Catalytic Converter System

Table 3.11 shows the emergy analysis of a catalytic converter based on a life span of 10 years. The main emergy inputs were grouped into: 1) platinum group metals, 2) construction materials and 3) mining and ecosystem losses. The rare metals (platinum and rhodium) accounted for 917E+12 sej. Fuel consumption for mining contributed 5861E+12 sej. Ecosystem losses due to mining added 12E+12 sej to the total emergy. The total emergy used to build the converter amounted to 8940E+12 sej (Table 3.11). The catalytic converter was estimated to remove 7.74E+5 g of CO over its lifetime (Appendix A). Therefore, the catalytic converter used 11.6E+9 sej/g of CO uptake.

The emergy requirement of the three CO-control technologies is summarized in Table 3.12. An increase in the scale of the lab-biofilter to a pilot-scale model reduced the sej/g by nearly two-orders of magnitude (Table 3.12). But the emergy needed by the catalytic converter is still lower than the pilot biofilter.

Table 3.11: Emergy evaluation of catalytic converter (10 year lifetime).

Note	Item	Unit	Value	Transformity ratios ETR MTR DTR	Emergy (sej) (E12)
18	Platinum	g	4.04	1.94E+14	784
19	Rhodium	g	0.69	1.94E+14	133
20	Cost	$	857	7.80E+11	669
21	Monolith Ceramic Support	g	8129	3.06E+09	25
22	Stainless Steel Can	g	9096	4.20E+09	38
23	Mining				
a)	Fuel	J	1.47E+11	4.00E+04	5861
b)	Ecosystem losses	g	4.73	5.89E+07	12
c)	Ore	g	1.42E+06	1.00E+09	1419
24	Total Inputs				8940
25	CO removed	g	7.74E+05		
26	Emergy used per gram of CO removed	sej/g		1.16E+10	

*- calculation for each note explained in Appendix C

Table 3.12: Summary of Emergy Analysis for Different CO Removal Technologies.

CO Removal Technology	CO Removed Over 10 yr life (g)	Inlet CO Concentration	Total Emergy Used (sej)	Emergy / g of CO Removed 1E9 sej/g
Lab Biofilter	661	~800 ppm	1.37E+15	2080
Pilot Biofilter	1.7E+7	~800 ppm	1.5E+18	85
Catalytic Converter	7.74E+5	4,800 ppm	8.86E1+5	12

3.2.4 Modeled Performance of Catalytic Converter at Lowered CO Concentration

Figure 3.22 shows the modeled catalytic converters performance over the range of 5 to 5,000 ppm-CO loading. Assuming the total emergy required by the catalytic converter remained constant, emergy per gram of mass removed was higher for lower treatment concentrations. At 800 ppm, which was the concentration of our biofilter, the catalytic converters required 40E+9 sej/g. This was half of the pilot-scale biofilter (85E9 sej/g). The pilot model was assumed to operate at the same specific CO-removal rate as the lab-scale model. CO removal may be higher at the industrial setup level, because of a larger media bed and more controlled conditions. Recent advances in biofiltration technology have lowered the EBCT to 10 seconds (BioReaction Inc., 2004). This is a factor of seven lower than the EBCT in our pilot model. The lower EBCT would allow a higher volume of CO to be treated for the same emergy requirements. This would result in a biofilter treating CO for 12E+9 sej/g (i.e., $1/7^{th}$ of 85E+9 sej/g, Table 3.13), which is lower than the catalytic converter operating at the same concentration. This indicates that the BF can remove CO for less total resources than the catalytic converters in the range of 500-1,000 ppm-CO. The question for future research is to determine the removal efficiency of the BF at inlet concentrations comparable to the engine exhaust. By scaling up the biofilters in terms of CO loading, the emergy per gram of CO removed may tend towards the more effective catalytic technology.

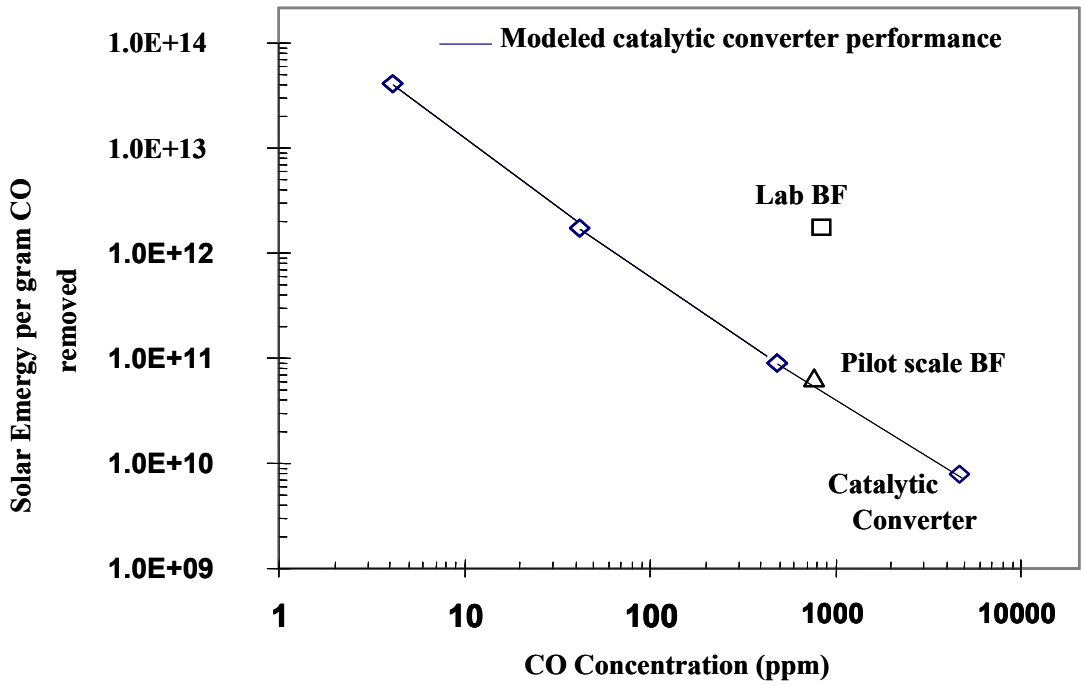


Figure 3.22: Solar emergy required by each of three treatment technologies to remove CO from a waste air stream as a function of inlet CO concentration.

Table 3.13: Summary of Emergy requirements of different CO control technologies

CO Removal Technology	CO Removed Over 10 yr life (g)	Inlet CO Concentration	Total Emergy Used (sej)	Emergy / g of CO Removed 1E9 sej/g
Lab BF	661	~800 ppm	1.37E+15	2080
Pilot BF, old	1.7E+7	~800 ppm	1.5E+18	85
Pilot BF, new (low EBCT)	1.25E+8	800 ppm	1.5E+18	12
Catalytic Converter	7.74E+5	4,800 ppm	8.86E+15	12
Catalytic Converter	2.21E+5	800 ppm	8.86E+15	40*

* From figure 3.22

Chapter 4: Discussions and Conclusions

Compost media showed higher CO removal than pebble media in my biofilter experiments and removed CO in both batch and continuous flow conditions. Biofilters were able to treat pure CO (bottled) as well as CO from an engine exhaust. Inoculations with soil slurries improved CO uptake considerably for both media. The compost biofilter adapted well to alternating operation and idle periods.

4.1 Biofiltration of CO

4.1.1 Elimination Capacity of Biofilters

Biofilters containing both organic (compost) and inorganic (pebble) media were shown to eliminate CO from air streams. The biofilters were able to remove CO from a CO-only air stream as well as from a mixed gaseous stream (engine exhaust). Table 4.1 shows my lab-scale study in perspective with some other recent advances in biofiltration of inorganic and organic pollutants. The CO biofiltration systems treated high CO concentrations at a very small flow rate as compared to the other studies.

Table 4.1 Recent biofiltration research advances in removal of organic and inorganic compounds

Pollutant	Pollutant Concentration	Media and Pollutant uptake by media	Flow rate	Author /Year
Hydrogen sulfide	100 ppm	10.8 g/m3/h	16.6 l/min	Jones et al, 2004
Formaldehyde	Not available	36.8 g/m3/h	2.5 l/min	Prado et al, 2004
Methanol	Not available	4.7 g/m3/h	2.5 l/min	Prado et al, 2004
Pure CO	1000 ppm	0.01 g/m3/h	0.5 l/min	Ganeshan, 2004 (this study)
Engine exhaust CO	1000 ppm	0.03 g/m3/h	1.3 l /min	Ganeshan, 2004 (this study)

4.1.2 Effect of Media, Inoculation, Loading and Chlorination on CO Removal

Media: Compost biofilter exhibited a greater capacity for removing CO overall. The batch/bottle experiments show that the compost biofilter, had significantly higher CO removal rates that the mineral biofilter for the 6-8 hour and the 8-24 hour exposures (Table 3.1). Eventually, at exposure times > than 24 hours both media were almost completely able to remove CO in the batch process. The co-efficient of uptake (k) for the different exposure times, also showed similar results as removal efficiency (Table 3.2). Models developed to predict compost and pebble CO removal also showed better CO removal performance by the compost biofilter. The compost biofilter showed quicker response to increasing exposure time (E_t) than the pebble biofilter (Figure 3.4), reaching steady state removal in 40 hours compared to over 100 hours taken by the pebble biofilter. The model response to increasing maturity time (M_t) (Figure 3.5) further consolidated the fact that compost was a better filter media. The compost biofilter (#6) was also effective in removing about 40% CO in the continuous/bottle experiment (Figure 3.7).

Under the continuous/engine experiments the compost biofilter removed more CO than the pebble biofilters. Compost biofilters demonstrated higher CO removal efficiencies (%) than the pebble biofilters for all tests. The comparison between CO-mass removed by the biofilters at the ~1000 CO ppm level (Figure 3.19) also demonstrated that the compost shows significantly higher (5% level) CO elimination capacity than the mineral biofilter. Figure 3.20 shows the mass removed by the compost and mineral biofilter at the ~ 700 CO ppm levels. The compost biofilter did significantly better than the mineral biofilter at the 5% level of significance during all

tests. The 3rd run on CM4 and PM1 showed no removal for both media. Figure 3.19 and 3.19 show that the compost biofilter removed a high of 0.565 mg of CO at a flow of 1.2 l/min at the 1000 ppm CO loading and 0.227 mg of CO at the ~700 ppm level. The pebble media removed a high of 0.291 mg of CO at the ~1000 ppm level and 0.034 mg of CO at the ~700 ppm level (Figure 3.19 and 3.20). These results show that the compost biofilter has a good capacity to remove CO from air streams. The anova analysis on the continuous/engine experiments (Table 3.7 and Table 3.8) show that the filter media and pollutant loading had a significant effect on CO mass removal form the biofilters.

The filter media is a key aspect in any biofiltration system, as it provides nutrients and support for microbial growth. The ideal media material should have high moisture holding capacity, porosity, available nutrients and pH buffer capacity (Leson and Winer, 1991). Compost is a good source of nitrogen and has been observed to be a good bed material for gas streams (Weckhuysen et al, 1993; Morgenroth et al, 1995). Mineral pebbles are inert and do not provide growth nutrients. The mineral biofilter could be exhibiting lower removal efficiency due to limiting nitrogen, while the compost being a good source of nitrogen could sustain high CO removal rates.

We have seen through the course of this study that compost has very good properties for a role as substrate or media. But it also suffers from some major drawbacks like pressure loss and compacting tendency. Easily biodegraded or un-rigid material like compost or peat suffers from aging, which leads to pressure drop across such media (Auria et al, 1998). Pebble media on the other hand maintains good

flow conditions but is nutrient lacking to provide a good microbial habitat. Biofilter media combining a nutrient rich material like compost and some inert media like clay pebbles could greatly improve removal efficiencies. Studies have shown that there was not significant difference in biofiltration removal capacities for different porous media like lava rock, perlite or activated carbon (Prado et al, 2004). BioReaction Inc. has come up with some innovative "Bio-ball" filter media, constructed of plastic and filled with compost. The plastic provides a large surface area and the compost serves as a nutrient rich substrate.

With constant nutrient and bacterial renewals, and methods to reduce preferential flow in media and increase bed contact, the compost biofilter showed very good promise to treat CO emissions. from a mixed pollutant air stream, as representative of industrial conditions. Also the mineral biofilter is lacking only in substrate. So a good quantity of nutrient rich media like compost would be a very good upgrade.

Inoculation: The biofiltration experiments have shown that inoculation has a positive effect on CO removal performance of both the compost and pebble biofilters. Fig 3.6 showed the performance of the compost biofilter (#6) during the continuous/bottle experiment. The steady state outlet at the beginning of the run, without inoculation does not show much reduction from the 1000 ppm inlet CO concentration. But with the first inoculation on day 5 there was a visible and clear reduction in CO ppm values (Figure 3.6) and an increase in CO removal efficiency (Figure 3.7). This shows that inoculation had a clear improving effect on biofilter performance. The improved performance of the biofilter stayed high for a few days

before showing higher CO outlet ppm and lower removal efficiency. A second inoculation again improved the biofilter performance, demonstrating the need for regular nutrient feed. After the inoculation experiments, the biofilter was operated under an "idle" mode, where no CO was passed through it for 35 days. The biofilter was again loaded with CO on day 70. The compost biofilter at the end of the first day's run showed reduced CO levels as before the start of the "idle" period. This high removal efficiency was maintained for 2 runs, before the steady state CO output started creeping up (Figure 3.6). This again signifies that the biofilter was nutrient starved. Table 3.4 shows the reduction in CO outlet levels between the different treatment periods. Each successive period recorded a lower CO outlet level than the previous, suggesting the improvement and acclimatizing properties of natural biofilter systems. The average mg of CO removed for each stage also showed an increasing trend (Figure 3.8), with the compost biofilter reaching levels of 0.203 mg of CO removal per hour at a flow rate of 0.5 l/min.

For the continuous/engine experiments almost all the biofilters showed a decline in CO removal after the 1st run (Table 3.5) except the compost biofilter operating at ~700 CO-inlet, which showed a slight increase in CO removal. The biofilters were inoculated with soil slurry and nutrients after the 2nd run, after which both the compost and mineral biofilters operating at ~1000 ppm inlet-CO, showed an improvement in CO removal. The compost and mineral biofilters operating at the ~700 ppm inlet-CO, both showed almost zero removal during the 3rd run. The fourth run again showed slightly reduced CO removal efficiencies, stressing the need for nutrient/bacterial inoculations.

Carbon, nitrogen and phosphorus are the main nutrients for microbial growth and metabolism. Carbon may be available to the microorganisms through the pollutant (organic pollutant). But nitrogen and phosphorus must be both provided by the filter media. Nitrogen makes up about 15% of cell mass (Carlson and Leiser, 1966) and hence can be a limiting nutrient for microbial activity. Although this study did not cover microbial interactions involved in carbon monoxide removal, its importance for effective removal cannot be underestimated. Microbial interactions can be severely inhibited due to nutrient limiting substrate. As microbes are responsible for CO uptake, it also becomes very important to maintain healthy microbial populations on media. Addition of inorganic nitrogen can significantly increase removal efficiency of biofilter (Weckhuysen et al, 1993). Prado (2004) has observed that best results were obtained for lava rock media that was renewed weekly with nutrient solution. Therefore, nitrogen and phosphorus formulas, in addition to soil slurry were added to both the compost and mineral lab biofilters. Soil slurry was added as innoculum to foster resident CO-oxidizing.

Loading: Pollutant loading levels seem to have some effect on biofilter performance. We have seen that compost biofilters exposed to higher CO concentration (~1000 ppm) have shown higher removal efficiencies than a compost biofilter exposed to lower CO concentration (~700 ppm). This tendency could result from microbial interactions, microbial count and media condition.

Chlorination: The effect of chlorination on biofilter performance was clearly understood by Figure 3.21, where chlorination effected almost 0% removal in

compost biofilter #6, treating CO at 104 ppm under continuous flow. The CO steady state value jumped from 65 ppm before disinfection to 97 ppm after chlorination.

4.2 Emergy Comparison of CO-Control Technologies

The biofilter was compared to the catalytic converter on the basis of environmental sustainability. Even though this study does not suggest replacing the catalytic converter with a biofilter, the emergy evaluation definitely helps to understand the importance of a sustainable pollution control technology. Table 3.12 shows the emergy per gram of CO removed for the different CO control technologies. Scaling up the lab-scale biofilter to a pilot-scale level greatly reduced its emergy requirements, because higher pollutant flows meant more treatment for the same emergy requirement. The pilot-scale biofilter with lower EBCT requires as much emergy as the catalytic converter treating CO at 4800 ppm and lesser emergy than the catalytic converter treating CO at 800 ppm. The improved biofiltration pilot model does much better than the catalytic converter in terms of emergy needs and CO removal. With more advances in biofiltration technology and innovation, this sustainability factor can only be improved. Also, research and development on the catalytic converter has been tremendous over the past 40 years, while biofiltration technology is only about two decades into wide-spread research.

Though the catalytic converter is very efficient in carbon monoxide removal, it causes severe environmental degradation and ecological losses. This approach to treating one pollutant and causing many more in the process has to give way to more holistic approach and design considerations

Traditionally, gas pollutants have been treated using physical and chemical processes like adsorption, condensation and incineration. (Kennes and Veiga, 2001). These technologies are relatively expensive and may produce undesirable side effects, like the generation of different toxic compounds (Deshusses,1997). In case of adsorption the pollutants are simply transferred from air to another phase. Currently, biofiltration is regarded as the best available control technology in treating diluted pollutants or odorous compounds because it is more cost effective than other technologies and minimizes generation of secondary contaminated waste streams (Gribbins and Loehr, 1998; Martinec et al, 2000; Elias et al, 2002). Biofiltration investment and operating costs are also lower than thermal and chemical oxidation processes (Govind, 1999; Paques,1997)

4.3 Summary of Conclusions

Conclusions from this research are summarized as follows- Traditionally, biofilters have been shown to remove VOC's at low loadings only. These studies show that Biofilters can be used to treat high loading of inorganic waste streams like CO.

1. The compost biofilters were able to remove ~90% of 1000 ppm (batch/bottle) in 24 hours. The pebble biofilters was able to remove 80% CO in the same time. The compost biofilters showed more accelerated removal during early exposure than the pebble biofilter.
2. Exposure time was a very important aspect and the models developed showed that compost media was able to achieve 100% removal in about 40 hours

while the pebble media would take more than 100 hours to completely remove CO. Maturity of the biofilters also played an important role in CO removal.

3. The compost biofilter (#6) attained about 40% removal of 1008 ppm of bottled CO under continuous/bottle experiments and removed 0.2 mg-CO/ hr at a flow rate of 0.5 l/hr.
4. The highest CO removal for the compost biofilter receiving engine exhaust at 1000 ppm was 45% after inoculation with soil and nutrients. Under 700 ppm-CO loading from engine exhaust, the compost biofilter removed a maximum of 17% CO. The pebble biofilter removed 20% CO at the 1000 ppm level and 4% at the 700 ppm level.
5. The highest CO mass uptake was 0.56 mg-CO/hr and 0.23mg-CO/hr for the compost biofilter at the 1000 ppm and 700 ppm levels respectively. The pebble biofilters removed a high 0.29 mg-CO/hr at the 1000 ppm level and 0.03 mg-CO/hr when receiving 700 ppm CO.
6. Filter media made a difference in biofilter treatment efficiencies. Compost media outperformed the pebble media in supporting CO elimination.
7. Adding soil and nutrient inoculations proved to improve and sustain removal of CO from both compost and pebble biofilters. We have observed in our experiments that soil inoculations were immediately followed by periods of high biofilter efficiency. Lab-scale biofiltration systems can be improved greatly by more frequent inoculations. Even greater efficiencies can be attained in a controlled industrial setting where microbial inoculations can be applied uniformly across media bed.

8. Chlorination of the compost media decreased CO uptake to almost 0%. This confirms the assumption that chlorination inhibited or killed microbes and the fact that CO degradation was microbial.
9. Emergy analysis shows that the biofilter can remove CO for less total resources than the catalytic converters in the range of 500-1,000 ppm-CO. Emergy serves as a powerful model to conduct environmental account and test sustainability of technologies.

4.4 Applications and Future work

Biofiltration is a relatively new but promising technology. Carbon monoxide biofilters can have very useful applications in enclosed automobile repair garages, where carbon monoxide levels can reach very levels. Carbon monoxide can also reach high levels in residences due to combustion devices. VOC's present in indoor environments also make the air unhealthy. As biofilters have also been proved useful to treat volatile organics, present in indoor air, small biofiltration units combined with foliage plants could provide cleaner and fresher ambience indoors. These units could be used in homes, offices, shopping-malls and even crowded trains to add aesthetic value along with an important utility. A biofilter treating carbon monoxide emissions could have a wide range of applicability in most industrial setups, requiring fuel combustion. The high concentrations of CO emitted from combustion exhausts could be effectively treated by biofiltration.

Some questions for future research are to determine the removal efficiency of the biofilter at CO inlet concentrations comparable to the engine exhaust and test optimum CO loading levels for a biofiltration setup. As CO biofiltration is microbial,

it will be a good idea to develop an experimental procedure to determine removal efficiencies of the biofilter at different CO concentrations and estimate optimum treatment concentrations for employing biofiltration. Also the biofilter could be used to target multiple pollutants in gaseous streams like engine exhaust and cigarette smoke. Testing a new media combining advantages of both pebble and compost materials could prove very effective in treating CO emissions.

Appendices

Appendix A: Carbon Monoxide Budget for Catalytic Converter

Energy equation for gasoline combustion can be described as:
$C_8H_{18} + 12.5\ O_2 \longrightarrow 8CO_2 + 9H_2O$, (Ebbing, 1993) I

The average fuel economy is 20 miles /gallon (USEPA, 1995c).
Average speed of car is assumed as 40 miles/hr. Therefore 2 gallons of gasoline is used up per hour by the average car.

1 gallon of gasoline (with MTBE) releases 117,960,000 J of energy (Chevron fact sheet, 2004)
Since 2 gallons are used up in 1 hour, energy /sec used up by the car = 65,520 J/sec

1 gallon of gasoline weighs 3,300 g
Molecular weight of gasoline -C_8H_{18} = 8x12 +18x1 = 114 g
Therefore 3,300 g (1 gallon) of gasoline releases 117,960,000 J of energy.
Therefore 1 mole of gasoline (114g) releases 4,074,981 J of energy.
To release 65,520 J /sec of energy, number of moles of gasoline required is?

1 mole	4,074,981 J
?	65,520 J

0.016 moles of gasoline releases 65,520 J
1 mole of gasoline requires 12.5 x 32(molecular weight of O_2) (Equation I)
= 400 g of O_2
Therefore 0.016 moles of gasoline requires 6.4 g of O_2.
Density of O_2 is 0.00131 g/cm^3
Therefore, volume of O_2 needed is 6.4/ 0.00131 = 4,885 cm^3 of O_2.
O_2 makes up 21 % of air. Therefore volume of air required to provide 4,885 cm^3 of oxygen will be (4885/ 0.21) = 23,260 cm^3/sec.

CO emissions per unit volume of air from Tailpipe are 0.19 % (Poulopoulos and Philippopoulos, 2000).
Therefore volume of CO emissions will be (0.19 x 23,260) / 100 = 44 cm^3.
Density of air is 0.00129 g/ cm^3 (Density of CO is almost equal to density of air)
CO emissions per sec is = 0.00129 x 44 = 0.057 g / sec, i.e. 57 mg/sec
The average life of a car is 100,000 miles.
Assuming the car runs at 40 miles /hr, average speed during its lifetime, number of hours a car runs is 2,500 hrs.

Therefore lifetime CO tailpipe emissions =57 x 60 x 60 x 2500 = 5.13E+8 mg of CO
i.e., 5.13E+5 g of CO.
CO emissions from engine (raw exhaust) per unit volume of air is 0.48% (Poulopoulos and Philippopoulos, 2000)
Therefore volume of CO emissions will be (0.48 x 23,260) / 100 = 111 cm^3.
Density of air is 0.00129 g/ cm^3. Therefore CO emissions is calculated to be = 0.00129 x 111 =143 mg/s
Raw engine emissions through lifetime of car = 143 x 60 x 60 x 2500 = 12.87E+8 mg, i.e. 10.41E+5 g.

Therefore CO treated by the Catalytic converter is = Raw engine emissions- Tailpipe emissions= 12.87E+5 – 5.13E+5 = 7.74 E+5 g of CO over lifetime.

Appendix B: Taylor Series Calculations for Biofilter Batch Flow model

Numerics for Non-linear Least Squares. (McCuen and Synder, 1986)

We wish to determine that unique set of values of the parameters such that the sum of the squares of the differences between the predicted and measured values of the criterion variable is a minimum.
The basic approach to non-linear solutions is based on Taylor series expansion of the models to be fitted. Consider the extremely simple function

$$Y_1 = f(X, a) \qquad \text{II}$$

Where the value of Y_1 is specified by one variable X and one coefficient a. Since we wish to find an optimum value of the coefficient a for a specific data set, $X's$ are fixed for that set but a can change from one sample point to another within a data set. The value of the objective function for a slightly different value of a, say $a + h$, would be

$$Y_2 = f(X, a + h) \qquad \text{III}$$

A Taylor series expansion would allow us to write

$$Y_2 = Y_1 + f'(X, a)\frac{h}{1!} + f''(X, a)\frac{h^2}{2!} + f'''(X, a)\frac{h^3}{3!} + R_n \qquad \text{IV}$$

Where $R_n = f^{(n)}(X, a_1)\dfrac{h^n}{n!}$ and $a \le a_1 \le a + h$

In practical numerical work, we do not usually need the highly precise expansion given by Equation IV
We are not interested in a single shift in our function from Y_1 to Y_2, caused by a single change h in the coefficient a. rather having shifted from Y_1 to Y_2 with a change h, we can now consider shifting from Y_2 to a new value Y_3 by an additional parameter change h. Finally if we keep h small, then h^2 and higher terms should be small enough to neglect in our successive shifts of the function. Hopefully, we can find some other manner of shifting until we find a value of the function Y which will produce the smallest residual sum of squares.
A Taylor series expansion is not limited to the simple form of one coefficient and one independent variate given by Equation IV. We might write the more general function as.

$$Y_1 = f(X_1, X_2, ..., X_m, a_1, a_2, ..., a_k)$$

$$Y_2 = f(X_m, a_1 + h_1, a_2 + h_2, ..., a_k + h_k)$$

If we limit the expansion to just the first differential, we obtain

$$Y_2 = f(X_m, a_1, a_2, ..., a_k) + h_1 \frac{\partial f}{\partial a_1} + h_2 \frac{\partial f}{\partial a_2} + ... + h_k \frac{\partial f}{\partial a_k}$$

If we had a function with four coefficients, we would write

$$Y_2 = Y_1 + h_1 \frac{\partial f}{\partial a_1} + h_2 \frac{\partial f}{\partial a_2} + h_3 \frac{.\partial f}{\partial a_3} + h_4 \frac{\partial f}{\partial a_4}$$

A simple rearrangement gives

$$E = Y_2 - Y_1 = h_1 \frac{\partial f}{\partial a_1} + h_2 \frac{\partial f}{\partial a_2} + h_3 \frac{\partial f}{\partial a_3} + h_4 \frac{\partial f}{\partial a_4}$$

Now consider Y_2 to be an observed value of our function. Then Y_1 can be considered the value predicted by the function for some value of the four coefficients a_i. But Equation says that by changing each of our coefficients by the appropriate h_i, we change the functional value from Y_1 to Y_2. This is the same as saying that we can adjust our coefficient to eliminate the error Y_2 - Y_1, or E_1

Appendix C: Footnotes to Tables 3.9, 3.10, and 3.11

Footnotes:

1 Compost/ soil - media in one biofilter.

Volume of Compost used per biofilter (calculated in lab)	0.0121	m^3
Life of Compost (assumed)=	3	yr
Therefore compost used for 10 years=		
(Volume of Compost)x(10 / Life of Compost)	0.0403	m^3
Density of compost (calculated in lab)=	480000.00	g/m^3
Organic fraction of compost (calculated in lab)=	0.50	g/g
Gibbs number for organic matter (Odum, 1996) =	22604.40	J/g
Potential energy stored compost (organic matter), (Odum, 1996)=		
Organic fraction (g/g) x Gibbs number (J/g) x Density(g/m^3) x Volume(m^3)		
Therefor Potential Energy stored in compost =	2.17E+08	J
Transformity for Compost (top soil ,organic matter) (Odum,1996)=	7.40E+04	sej/J

2 PVC requirement

Weight of plastic pipes used in biofilter construction (calculated in lab)=	3.54	lbs/ ft
Therefore 3 ft biofilter requirement =		
3x (Unit weight of Plastic/ft)	10.61	lbs
Life of plastic pipes (assumed)=	10.00	years
Therefore PVC requirement for 10 years=		
(Plastic requirement per biofilter)x(10/Life of plastic)	4.80	kg
Transformity for PVC (Buranakarn, 1998)=	5.90E+09	sej/g

3 Electricity used: vacumn pump to maintain flow through conditions

Vacumn pump rating (specification)=	0.33	HP
=	248.67	J/sec
Assuming 8 hr a day operation, 5 days a week for 10 years		
Hours operated in 10 years=		
8hours x 5days/week x 52weeks/year x 10years	20800.00	hours
Energy consumed by 6 biofilters	1.86E+10	
Therefore energy consumed by 1 biofilter=	3.10E+09	
Transformiy for electricity (Odum,1996)=	1.70E+05	sej/J

4 Wood needed for Biofilter bench

Total quantity of wood needed to setup 6 biofilters(calculated) =	38.00	kg
Wood requirement for 1 biofilter =	6.33	kg
Life of wood setup=.	10.00	years
Wood needed for biofilter for 10year lifetime=		
(Wood requirement for 1 biofilter)x(10/lifetime of wood setup) =	6.33	kg
Transformity for wood (soft plywood) (Buranakarn, 1998) =	1.21E+09	sej/g

5 Steel needed for Biofilter support

Total amount of steel needed to setup 6 biofilters =	20.00	kg
Life of steel support=	10.00	years
Therefore steel for 1 biofilter =		
(Total steel requirement) / (No. Biofilters)		
(Steel requirement for 1 biofilter) x (10/lifetime of steel setup) =	3.33	kg
Transformity for Steel (Buranakarn, 1998) =	4.20E+09	sej/g

6 Labor to build Biofilters

Number of hours needed to build the setup =	52.00	hours
Project charge / hour=	45.00	$
Total cost =	2340.00	$
Life of setup	10.00	years
Cost of setup for 1 biofilter =	390.00	$
Transformity of the US dollar (Tilley, 2004)=	7.80E+11	sej/$

7 Material costs for 6 biofilters

Item	**Cost ($)**	
Valves	305.92	
TYGON tubing	188.46	
Reducer connectors	1.14	
Hose nylon Elbow	7.50	
stopcocks	701.96	
5 gallon buckets	32.70	
Flowmeters	1482.00	
PVC pipes	941.20	
TOTAL	**3660.88**	
Material life (assumed)=	10.00	years
Cost for 1 Biofilter=		
Total cost/ 6	610.15	$
Transformity of the US dollar (Tilley, 2004)=	7.80E+11	sej/$

8 Total Emergy spent over the lifetime of the Biofilter

Total Emergy =	1374	E12 sej
(sum of items from 1 through 7)		

9 CO removed

CO removed is (see results section) =	0.53	mg/min
No. hours operated (8hr day 5 day/week operation)=	20800	hours
Therefore CO removed over 10 year life of Biofilter=	661.44	g
(CO removal rate, mg/min)x(Hours of operation, hours)x 60 min/hr		

10 Emergy of Biofilter per g of CO removed

Total emergy of biofilter setup=	1373.70	E12 sej

CO removed over 10 year life =	661.44	g
Therefore Emergy of biofilter/g of CO removed =		
Total emergy / CO removed	2.08	E 12 sej

11 Compost/ soil is used as the media in the biofilters.

Volume of Compost per biofilter(from case study), (DeVinney,1999)	314.00	m^3
Life of Compost (DeVinney, 1999)=	3	years
Therefore compost used for 10 years =	1045.62	m^3
Density of compost (calculated in lab)=	4.80E+05	g/m^3
Organic fraction of compost (calculated in lab)=	0.50	g/g
Gibbs number (Odum, 1996) =	22604.40	J/g
Potential energy stored compost (odum,1996)=		
Organic fraction (g/g) x Gibbs number (J/g) x Density(g/m^3) x Volume(m^3)		
Therefore Potential energy stored in compost =	5.62E+12	J
Transformity of compost (organic matter), (Odum 1996)=	7.40E+04	sej/J

12 Electricity used: Centrifugal pump to maintain flow through conditions

Centrifugal pump rating, case study (DeVinney, 1999))=	40.00	HP
=	29840.00	J/sec
Assuming 8 hr a day operation, 5 days a week for 10 years		
Hours operated in 10 years=	20800.00	hours
Energy consumed by pilot scale biofilter	2.23E+12	J
Transformiy for electricity (Odum, 1996)=	1.70E+05	sej/J

13 Initial Investment

including setup, material costs and auxillary equipment	550000	$
Transformity for US dollar (Tilley, 2004)=	7.80E+11	sej/$

14 Maintenance costs

Maintenace + other operating costs per 1000 m^3 gas treated (DeVinney, 1999)	0.83	$
Treatment, from case study, (DeVinney,1999)	17000	m^3/hr
Hours of operation for 10 years= (8 x5 x 52 x10)	20800	hrs
Total cost=	293488	$
Transformity for US dollar (Tilley, 2004)=	7.80E+11	sej/$

15 Total Emergy

Sum 1 to 4=	1453342.70	sej

16 CO treated

Lab scale biofilter volume =	0.0121	m^3

Lab scale CO removal (Results Section)=	0.53	mg/min
Pilot scale biofilter volume =	314	m^3
Pilot scale CO removal= [(pilot scale volume) x (Lab scale removal)] / (lab scale volume)		
(assuming pilot scale model has same removal efficiency as lab scale model)		
Therefore CO removal by pilot model =	1.38E+04	mg/min
Hours of operation=	20800	hr
Therefore CO removed in 20800 hours=	1.72E+07	g

17 Emergy /g of CO removed

Total emergy =	1.45334E+18	
CO removed =	1.72E+07	
Emergy/ g removed =	8.47E+10	

1) Platinum

Amount of Platinum used in a catalytic converter (life 7yr) (Taylor,1987)	2.83	g
Therefore usage in 10 years	4.04	g
Transformity of Platinum (metal formation) (Odum and Brown,1993)=	1.94E+14	sej/g

2) Rhodium

Amount of Rhodium used in a catalytic converter (life 7yr),(Taylor,1987)	0.48	g
Therefore usage in 10 years	0.69	g
Transformity of Rhodium (metal formation), (Odum and Brown, 1993)=	1.94E+14	sej/g

Transformity is also assumed 1.94e14 sej/g, -the same as platinum, as a number for rhodium is unavailable. This estimate is on the lower side as Rhodium availability is low and it is more expensive than platinum or palladium.(Taylor,1987)

3) Cost of a Catalytic converter

Cost =	600	$
Life of a catalytic converter (assumed)=	7	years
Usage in 10 years (cost)	857	$
Transformity for the US dollar (Tilley,2004)=	7.80E+11	Sej/$

4) Monolith Ceramic support

This is the substrate over which a coating of the platinum metals is applied. The substrate is in the form of 2 bricks

No. substrate bricks in a Catalytic converter (Burch et al, 1996)=	2	nos
Diameter of brick (Burch et al, 1996)=	144	mm
Length (Burch et al, 1996)=	76	mm
The total volume of the 2 cylindrical bricks=	2474	cm^3

The ceramic substrate is made of Cordierite (2Mg, 2Al203, 5SiO2), (Burch et al, 1996)

Material density of cordierite (Environmental Technology Co., China)=	2.3	g/cm^3
Mass of cordierite used in 7 year life=	5690.70	g
Mass of cordierite used in 10 year life=	8129.58	g
Transformity of Cordierite, similar to ceramic (Buranakarn, 1998) =	3.06E+09	sej/g

5) Stainless steel can

Stainless steel is used as a housing for the catalytic converter

Dimensions of the cylindrical stainless steel body		
Diameter of Steel housing (Burch et al, 1996)=	216	mm
Length of steel housing (Burch et al, 1996)=	490	mm
Surface area of the cylinder =	0.41	m^2
Thickness of metal sheeting (assumed)=	2	mm
Volume =	0.0008	m^3
Density of steel=	7850	kg/m^3
Therefore, mass of steel used for 7 year life=	6.37	kg
Therefore, mass of steel used for 10 year life=	9.10	kg
Transformity of stainless steel (Buranakarn, 1998) =	4.20E+09	sej/g

6a) Fuel used for mining

Nonrenewable resources used to mine 1g of rare metal =	1000	kgs
(Friedrich Schmidt-Bleek, Unpublished data, 2001)		
This includes cost of mining, smetling etc.		
Coal is assumed to be most of the raw material used.		
Energy obtained form 1g of coal =	30976.4	J
Energy obtained form 1000 kgs of coal =	3.10E+10	J
Therefore 1 g of rare metal mined needs 3.10e10 J of energy		
A catalytic converter uses 2.83 g of platinum + 0.48g of Rhodium		
Total rare metal used for one catalytic converter (10 year use)=	4.73	g
Therefore energy used in mining to build one catalytic converter =	1.47E+11	J
Transformity of fuel =	4.00E+04	

6b) Ecosystem loss in productivity

Forest loss in Norlisk, large rare metal mine in Russia (Kiseleva, 1996) =	61303	ha
Emergy of forest formation lost (Odum, 1996)=	7.00E+14	Sej/ha/year
No. of years for forests to degrade completely (assume)	20	years
No. of years for forests to regain original productivity (assume)	200	years
Total Emergy lost = Gradual emergy loss till complete (linear) degradation(20yr) + productivity lost during grow back period(200yr).	4.72E+21	sej
Total production of platinum + palladium 1970 to 1990	1900000	kg
(Norilsk produces 700000 oz of platinum and 2.8 Moz of palladium each year)		
Therefore emergy lost per g of platinum mined	2.48E+12	Sej /g
Rare metals used / catalytic converter (7 year life)	3.31	g
Rare metals used / catalytic converter (10 year life)	4.73	g

6c) Ore

Ore used to mine 1g of rare metal =	300	kg
(Rienier de Man, Unpublished data)		
Rare metals used / catalytic converter (10 year life)	4.73	g
ore use to mine 4.73 g of raremetal used for one catalytic converter =	1418.57	kg
Transformity of ore =	1.00E+09	Sej/g

7) Total inputs

Sum of inputs points 1 to 6	8940	

8) CO removed

CO removed by the catalytic converter over 10 year life (Appendix A)	7.74E+05	g

9) Emergy per g of CO removed

Total emergy of catalytic converter=	8.94E+15	sej
CO removed	7.74E+05	g
Emergy per g of CO removed	1.16E+10	sej/g

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